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APPLICATION OF INNOVATIVE METHODS OF SOURCE APPORTIONMENTIN AIR CONTAMINATION ASSESSMENT

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Alla mia mamma, al mio babbo, alla Nena

e alla mia nonna, che se fosse ancora qui

si stimerebbe tutta perché.

“La su Elisa la chapana roba

ancor piùgrosadla laurea”

Abstract

In this work, new tools in atmospheric pollutant sampling and analysis were applied in order to go deeper in source apportionment study. The project was developed mainly by the study of atmospheric emission sources in a suburban area influenced by a municipal solid waste incinerator (MSWI), a medium-sized coastal tourist town and a motorway. Two main research lines were followed. For what concerns the first line, the potentiality of the use of PM samplers coupled with a wind select sensor was assessed. Results showed that they may be a valid support in source apportionment studies. However, meteorological and territorial conditions could strongly affect the results. Moreover, new markers were investigated, particularly focusing on the processes of biomass burning. OC revealed a good biomass combustion process indicator, as well as all determined organic compounds. Among metals, lead and aluminium are well related to the biomass combustion. Surprisingly PM was not enriched of potassium during bonfire event.

The second research line consists on the application of Positive Matrix factorization (PMF), a new statistical tool in data analysis. This new technique was applied to datasets which refer to different time resolution data. PMF application to atmospheric deposition fluxes identified six main sources affecting the area. The incinerator's relative contribution seemed to be negligible. PMF analysis was then applied to $PM_{2.5}$ collected with samplers coupled with a wind select sensor. The higher number of determined environmental indicators allowed to obtain more detailed results on the sources affecting the area. Vehicular traffic revealed the source of greatest concern for the study area. Also in this case, incinerator's relative contribution seemed to be negligible. Finally, the application of PMF analysis to hourly aerosol data demonstrated that the higher the temporal resolution of the data was, the more the source profiles were close to the real one.

Keywords

atmospheric pollution; source apportionment; Positive Matrix Factorization (PMF); selective sampling device; open fire; Municipal Solid Waste Incinerator

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AIM OF THE WORK

Whenever a not developed country has undertaken industrial development, its air quality has significantly worsened.

The better known example of air pollution is photochemical smog, especially due to compounds emitted by vehicle tailpipes. Among human activities, this is the main cause of air pollution[1]; nevertheless there are other important sources, such as industrial activities, energy production, domestic heating.

As a consequence urban areas are interested by remarkable health problems due to the inhalation exposition of the population. Moreover global warming and climate change due to greenhouse effects and air pollution continue to be serious problems; therefore how to effectively improve the combustion efficiency and mitigate the emissions of greenhouse gases and other pollutants becomes an international and imperative issue[2].

One of the first reference to sustainable development can be found in a declaration of the Council of the European Community (1973);inthe first programme of action on environment, it is stated that "*expansion should be into the service of man by procuring for him an environment providing the best conditions of life, and reconcile this expansion with the increasingly imperative need to preserve the natural environment.*"[3] Consequently, governments started to legislate in order to reduce the impact of human activities on the environment. The firstairquality limit and guide values for some pollutants (sulfur dioxide and suspended particulates)were fixed in 1980, with 80/779/CEE directive[4].

Over the years air quality laws became more and more stringent. Scientific researchers worked on one side to make the impact of pollution sources on the environment lower and lower, on the other side they tried to assess the contribution that each emission source

makes on the environment, in order to set the sources it is necessary to operate on the most to reduce air pollution. In this contest my PhD research project takes places.

The project consists on the development and the application of innovative source apportionment methods, in order to identify the contribution of different emission sources to the total pollutant amount, particularly focusing on industrial. Indeed a detailed understanding of the nature and origin of pollutants is important in order to identify the relative importance of emission sources, to investigate the associations between specific components and health, and for policy makers to introduce suitable legislation for its control[5].

Since atmospheric particulate matter (PM) can sorb many pollutants such as heavy metals, acidity oxide, organic pollutants, virus etc. and it is of concern for both environmental and health reasons[6], the most of the study is focused on this environmental matrix.

The project is developed mainly by the study of atmospheric emission sources in a suburban area influenced by a municipal solid waste incinerator (MSWI), a medium-sized coastal tourist town and a motorway. This area has been chosen since having an area with several emission sources which affect air pollution is a common situation. Therefore the results obtained in this PhD research project can be useful to generally try to solve air pollution related problems.

PM sampling and analysis is nowadays a very common and spread practice to assess air pollution. In this work, new tools have been applied in order to go deeper in source apportionment study. Two main lines have been followed. On one side,new sampling approaches and new markerswere studied. On the other, new statistical tools in data analysis wereapplied. Results of the first research line are discussed in Section I, whereas Section II deals with the second research line.

Specifically, for what concerns the first research line, the potentiality of the use of samplers coupled with a wind select sensor, in order to sample only the air masses influenced by specific emission sources, was assessed, since it is still little used. Among the several possible approaches, this allows a predefined selection of samples, influenced by specific sources, even if they are collected at the same site. For this reason a smaller number of samples should be sufficient to define the contribution of the sources.[7].

Moreover, new specific markers have been investigated in order to obtain more complete and quantitative information on the sources affecting the area.Among the several natural and anthropogenic sources of atmospheric aerosol, there is a growing attention on the processes of biomass burning, which include residential burning of wood or pellets for household heating and open fires for the reduction of agricultural debris[8]. Although biomass combustions markers are well known, because of the high variability, few studies assess the quantitative contribution of these sources to PM concentration[9]. In order to estimate the airborne particulate matter contribution due to open fires, and to go deeper into the markers of outdoor biomass burning, total suspended particulate (TSP), PM_{10} and $PM_{2.5}$ were collected before, during and after Saint Joseph eve (18th of March). On this day, huge bonfires, called "Fogheracce", are usually ignited in this area, in order to welcome spring.

Even if these studies provided useful information on the sources affecting the area, results cannot give quantitative and complete responses on the causes of air pollution in the area. The implementation of data analysis with new and more powerful statistical tools (second research line) can finally reach this aim.

Chemometric methodsare very spread and useful in data analysis of complex dataset, since they allow to colleague contaminants related to the same source. Positive Matrix factorization (PMF) is a new approach compared to Principal Component Analysis (PCA); it is more powerful and provides quantitative information on source contributions.It has several advantages for the applications in environmental studies. First of all measure uncertainties and below detection limit data can be managed. But the most important characteristic is that loadings matrix has only positive values and this is a fundamental feature in source apportionment studies, where each factor should represent a different emission source[10,11].This new technique has been applied to datasets which refer to different time resolution data.

- Atmospheric bulk deposition, an environmental matrix which serves mainly the following purposes: analysis of temporal and spatial trends and need for a fundamental understanding of mechanisms transferring chemical constituents from the atmosphere to surfaces[12,13].
- PM collected with samplers coupled with a wind select sensor, in order to sample only the air masses influenced by specific emission sources. Our previous work

proved that this technique by itself is not enough to quantitatively assess the contribution of the several emission sources, especially in little contaminated areas. Therefore a new campaign was undertaken, more samples were collected and more analytes were determined, in order to obtain a dataset suitable for the PMF.

- Hourly aerosol data obtained with online methods in an urban site. The high time resolution chemical composition of atmospheric aerosol aids the source apportionment studies by capturing dynamic processes related to source activity.

Thanks to this work, it will be possible to have a complete overview on the potentiality of the technique when it was applied to different kind of dataset.

Finally, thanks to the combination of the application of PMF with the previous assessed tools (samplers coupled with a wind select sensor and bonfire markers), the study aims to quantitatively assess the contribution of the emission sources.

Section I

ATMOSPHERIC PARTICULATE MATTER: NEW SAMPLING APPROACHES AND NEW MARKER STUDY

1 Atmospheric particulate matter

1.1 PARTICULATE MATTER DEFINITION

The United States Environmental Protection Agency (US EPA), defines atmospheric particulate matter not as an individual pollutant, but as a complex mixture of different chemical components which exist as a suspension of solid or liquid particles in air, with a wide dimension range.

Particulate dimensions are included between 2 nm and 100 µm. Particles greater than 100 µm can be difficultly found in atmosphere because, since their mass, they settle rapidly to the ground, whereas 2 nm can be considered the upper limit of gas phase molecules.

Chemical and physical proprieties of particulate depend on the emission source and on the transformation it undergoes during its stay in the atmosphere[14].

1.2 PARTICULATE MATTER CLASSIFICATION

Despite atmospheric particles often are not spherical, referring to them as they were spherical is a common convention. Particulate diameter is its main propriety[1]. Diameters are describedby an “equivalent” diameter (i.e., the diameter of a sphere that would have the same physicalbehavior). There are several diameter definitions, depending on the considered physical characteristic: optical, mobility, Stoke and aerodynamic diameter. For the purposes of this study, only aerodynamic diameter definition will be considered. The aerodynamic diameter, D_a, depends on particle density. It is defined as the diameter of a spherical particle with an equal gravitational settling velocity but a material density of 1 g/cm^3.

The particulate matter classification is based on particle size or origin. Aerosol scientists use three different approaches or conventions in theclassification of particles by size: modal, dosimetricand cut point.

Modal classification. It was first proposed by Whitby (1978) and it is based on the observed size distributions and formation mechanisms. There are two main classes:

- *Fine Particles:* particles from the lowest measurable size, currently about 3 nm, to just above the minimum in the mass or volume distribution which generally occurs between 1 and 3 μm.
- *Coarse Mode or Coarse Particles:* Particles with diameters mostly greater than the minimum in the particle mass or volume distributions, which generally occurs between 1 and 3 μm.

Ultrafine Particles are not a mode. In the air pollution literature, they are generally defined by size alone, i.e., particles with diameters of 0.1 μm (100 nm) or less.

Occupational Health or Dosimetric Size Cuts. It is based on the entrance into various compartments of the respiratory system, so it is used to evaluate particulate interaction with human. USEPA has chosen this convention, which classifies particles into inhalable, thoracic, and respirable particles according to their upper size cuts.

- *Inhalable particles:* particles with a diameter greater than 5.8 μm, which enter the respiratory tract, beginning with the head airways.
- *Thoracic particles:* particles with a diameter between 5.8 and 3.3μm, which travel past the larynx and reach the lung airways and the gas-exchange regions of the lung.
- *Respirable particles:* particles with a diameter lower than 3.3 μm which are more likely to reach the gas-exchange region of the lung.

Cut point. It is based on the 50% cut point of the specific sampling device, including legally specified, regulatory cut points for air quality standards. Size-selective sampling refers to the collection of particles below or within a specified aerodynamic size range with a sampler with inertial impaction. Size fractions are usually specified by the 50% cut point size; e.g., $PM_{2.5}$ refers to particles collected by a sampling device that collects 50% of 2.5 μm particles and rejects 50% of 2.5 μm particles. PM_{10}, as defined by EPA, refers to particles collected by a sampler with an upper 50% cut point of 10 μm D_a. The resulting $PM_{10\text{-}2.5}$ mass, or $PM_{10\text{-}2.5}$, is sometimes called “coarse” particles or “thoracic coarse” particles. Also, $PM_{2.5}$ should be considered an indicator of fine particles and sometimes they are called “respirable” particles. This class can represent up to the 85% of PM_{10}[15].

Based on the design of the sampler is also Total Suspended Particulate (TSP) definition. The upper cut-off size of the sampler depends on the wind speed and direction and may vary from 25 to 40 μm. Newer PM samplers are usually designed to have an upper cut point and its standard deviation that are independent of wind direction and relatively independent of wind speed.The resulting PM_{TSP-10} is sometimes called "ultra-coarse" particles.

Atmospheric particulate matter can be classified on the basis of the origin in:

Anthropogenic particulate: it is due to human activities, or by direct emission (e. g. particles from combustion processes) or by chemical transformation of parent compounds (e. g. NO_x)

Natural particulate: it is due to natural material transformation or to direct emission by natural sources[1].

Or on the basis of production process in:

Primary particulate: it is in the same chemical form in which it was emitted into the atmosphere,

Secondary particulate: it is formed by chemical reactions in the atmosphere. They include photochemical reactions or oxidation processes of parent compounds (ammonia, reactive volatile organic compounds (VOC), NO_x, SO_x). These events are more intensive when temperature and solar radiation are high. In general, all the reactions between gaseous compounds and the surface or core of particles with a diameter greater than 0.1 μm form this kind of atmospheric particulate[14]

1.3 PARTICULATE MATTER CHEMICAL COMPOSITION

Since different sources emit different chemical compounds and particulate dimension depends on the emission source, chemical composition depends also on dimensional classes.

Coarse particles are usually formed by mechanical processes (erosions, frictions, sea salt evaporation, windblown dust, road dust re-suspension). Despite the most of coarse

particle has a natural origin (marine salt aerosol, soil dust and natural fire debris), some human activities, such as crushing stones or soil-growing, cause wind driven resuspension of stone particles and superficial soil[14].

Fine particles are principally constituted by incomplete combustion products and secondary PM and they have a strong anthropogenic influence. Primary particles can be found both in fine and coarse fraction, while secondary particles can be found mainly in the fine fraction[1].

Sulfates: natural sulfur can be found in the air mainly as sulfide dioxide (SO_2), which is originated by the oxidation of dimethyl sulfur $(CH_3)_2S$, a compound emitted from the oceans. Furthermore it is emitted directly from natural sources, such as volcanos, and it is produced by thermal power stations and foundries. In the air, it is oxidized to sulfuric acid, which forms fine droplet aerosol[1].

Nitrates: they are the oxidation product of NO_2 and NO, which are emitted especially by anthropogenic sources, such as combustion processes. They are one of the most important secondary $PM_{2.5}$ components[1].

Ammonium: it is mainly due to biogenic ammonia salification with nitric and sulfuric acid, but it can also be due to the use of ammonia fertilizer and to industrial sources[1].

Crustal degradation elements (aluminum, silicon, calcium, titanium, iron and other metal oxides): concentrations depend on soil geology and on the state of soil surface, on climate and on suspension processes[16].

Marine spray elements (Na^+, Cl^-, Mg^{2+} and SO_4^{2-}): above oceans, solid NaCl concentration is very high, since marine spray produces sodium chloride particles suspended in the air, after water evaporation. Sodium is a conservative element in seawater and its origin is less ambiguous than other atmospheric aerosol components, therefore it is very useful in order to evaluate sea fraction contribution[1].

Trace elements, metals and non-metals: they can be found in particles with different dimensions, which strongly depend on the emission source. Fine fraction metals originate from coal and oil burning impurities which vaporize during the combustion. They can also be emitted by municipal waste incinerators and by vehicular exhaust pipes. Coarse

fraction metals can be released by car brake, biomass burning, mineral extraction and working processes, foundries and ceramic industries[16].

Elemental Carbon (EC): it is the fraction of carbonaceous particulate which does not oxidize at a temperature lower than 400°C. Its origin is primary; it is due to the incomplete combustion of fossil fuels. Therefore, one of its main sources is vehicular exhausts, especially of cars with diesel engine. About an half of carbon content of heavy diesel vehicles exhausts is elemental carbon, while most of carbon exhausts from gasoline engine vehicle is organic carbon[14,17]

Organic carbon (OC): it represents about 60-80% of the total carbon and it is constituted by a mixture of hydrocarbons and oxygenated compounds, e.g. polycyclic aromatic hydrocarbons (PAH) and dioxins. Organic aerosol can have a primary origin, it is formed during combustion processes and is emitted mainly as submicron particles, and a secondary origin. In traffic congested areas, up to an half of organic compounds of the particulate are hydrocarbons. The mean content of organic matter in fine particulate is higher than in coarse particles[16,17]

Polycyclic Aromatic hydrocarbons: these compounds are usually present in air in different proportion, depending on their main sources. They are mainly found in submicron particles. They have both a natural and an anthropogenic origin, but the main contribution is made by human activities. They can be divided in two categories:

Pyrogenic PAH: they are formed during high temperature combustion processes; their emission sources are vehicular traffic, industrial productions (carbon coke, charcoal, aluminum), domestic heating and electric power plants

Petrogenic PAH: they are present in petroleum and in its derivatives and they are emitted by fossil fuel handling[1]

Levoglucosan (1,6-anhydro-β-D-glucopyranose): it is formed during cellulose pyrolysis and it is a specific marker of biomass combustion. It can be found only in fine particulate[8]

Biological components: they are constituted by bacteria, pollen and other vegetal and animal fragments. They can be found in coarse particle and their origin is primary[16]

1.4 REGULATIONS

As reported previously, the first air quality limit values for suspended particulates were fixed in 1980, with 80/779/CEE directive[4]. It refers to TSP and fixes a median yearly value of 80 µg/m^3 if TSP is measured with black smoke method and a mean yearly value of 150 µg/m^3 if it is measured with the gravimetric method. The 98 percentile of all daily mean values must be 250 µg/m^3 for black-smoke method and the 95 percentile of all daily mean values must be 350 µg/m^3 for gravimetric method. For the black-smoke method, guide values are also indicated: the mean yearly value should range from 40 to 60 µg/m^3, while daily mean value should range between 100 and 150 µg/m^3. With 1999/30/CE[18] directive, TSP is substituted with PM_{10}. Limit values become much stricter. Mean yearly value is fixed to 40 µg/m^3 up to 2005 (first phase) and to 20 µg/m^3 after (second phase). Daily mean value is 50 µg/m^3. It is allowed to exceed this value 35 times a year up to 2005, while only 7 times after. The reference method is the gravimetric, as described in EN 12341 method. With 2008/50/CE[19] directive limit values for PM_{10} of the first phase of 1999 directive were confirmed and limit values for $PM_{2.5}$ were added. For the first phase, mean yearly value is fixed to 25 µg/m^3, while it is 20 µg/m^3 for the second phase. This value is indicative and should be reviewed in 2013, in the light of further information on health and environmental effects, technical feasibility and experience of the target value in Member States.

Lead is a well-known toxic metal which is present in PM. In Europe, it is regulated since 1982. 82/884/CEE[20] directive fixes the mean yearly value to 2 µg/m^3; this concentration is referred to PM_{10}. With 1999/30/CE[18] directive, limit value became stricter, 0.5 µg/m^3. 2008/50/CE[19] directive confirmed this limit value.

Finally 2004/107/CE[21] directive fixes mean yearly target values for As, Cd, Benzo(a)Pyrene and Ni in PM_{10}: 6, 5, 1 and 20 ng/m^3 respectively. Actual and past mean yearly limit values are summarized in Table 1.1.

Table 1.1: Mean yearly limit values for TSP, PM_{10}, $PM_{2.5}$, Pb, As, Cd, Benzo(a)Pyrene and Ni in past and present European directives

	TSP	PM_{10}	$PM_{2.5}$	Pb (PM_{10})	As (PM_{10})	Cd (PM_{10})	B(a)P (PM_{10})	Ni (PM_{10})
80/779/CEE	80 µg/m^{3*} 150 µg/m$^{3\#}$							
82/884/CEE				2 µg/m^3				
1999/30/CE		40 µg/m$^{3§\#}$ 20 µg/m$^{3\sim\#}$		0.5 µg/m^3				
2004/107/CE					6 ng/m$^{3¤}$	5 ng/m$^{3¤}$	1 ng/m$^{3¤}$	20 ng/m$^{3¤}$
2008/50/CE		40 µg/m^3	25 µg/m^{3§} 20 µg/m$^{3\sim}$	0.5 µg/m^3				

* Black smoke method
# Gravimetric method
§ First phase
~ Second phase
¤ Target value

2 Source apportionment study based on selective wind direction sampling

2.1 EXPERIMENTAL METHODS

2.1.1 Sampling site

The sampling site is located in a city park, on a 60 m ASL hill ridge (Figure 2.1), in the southwestern suburban area of the medium-sized tourist town of Riccione (RN) (35 000 inhabitants). The two principal wind directions are southwest and northeast (land and sea breeze), roughly perpendicular to the coast line. Consequently the site is alternatively downwind of the costal urban area and of the hinterland, which is mainly characterized by the presence of a Municipal Solid Waste Incinerator (MSWI) and a motorway. The industrial plant is 2 km away from the sampling site; it has been in operation since 1976 and it is authorized to burn 140 000 t of urban and hospital solid waste per year (maximum 1000 t/ year of the latter); the emission stack is 40 m tall. Initially equipped with two separate incineration lines able to treat 120 t of municipal solid waste (MSW) per day each, plant capacity was increased of 200 t per day with a third line in 1992. From February 2008, the plant was revamped, with the construction of a new incineration line and the dismantling of the oldest ones[22].

The A14 motorway is about 600 m away and runs roughly 30 m below the sampling site. It is used by an average of 60000 vehicles per day.

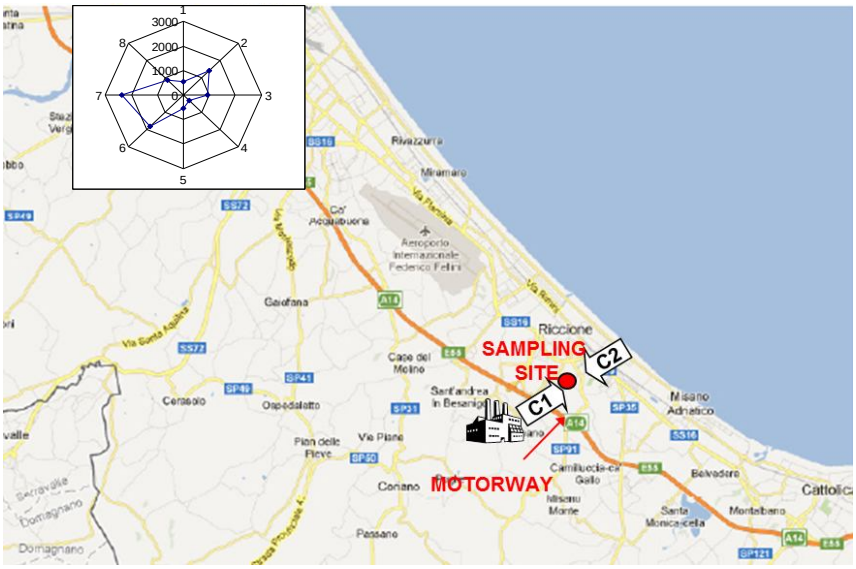

Figure 2.1: Sampling site and principal wind direction in the area (from © 2011 Google – Immagini © 2011 [ena] – modified).

2.1.2 Sampling

Two medium volume samplers (Skypost PM, TCR TECORA), equipped with a PM_{10} sampling head, were used. Each sampler operated at the flow rate of 38.33 l/min. The samplers were coupled with a wind direction sensor, which allows the turning on and off of the instrument depending on wind direction. The first sampler (C1) collected PM_{10} coming from inland, that was thus influenced by the incinerator and the motorway. The sampler switched on when it was downwind of the incinerator ±60° (120 degree window). The second sampler (C2) collected PM_{10} coming from the coast, that was thus influenced by the urban area. The sampler turned on when it was downwind of the coast ±90° (180 degree window).

Two sampling campaigns were performed, the first one in the autumn (from 26th October to 30th November 2009) and the second one in the spring (from 17th May to 20th June 2010). Overall, 32 samples were collected (20 in the autumn and 16 in the spring).

Each sampling lasted 72 hours, so 2 samples a week were collected. In order to assess differences between midweek (m) and weekend (w) days, the first weekly sampling began on Monday, at 12:00 a.m. and finished on Thursday, at 12:00 a.m. The second one began on Friday at 00:01 a.m., and finished on Sunday at 11:59 p.m.

2.1.3 PM_{10} quantification

PM_{10} samples were collected on quartz fiber filters (SKC, 47 mm diameter). Before use, the filters were baked at 200°C for an hour. Filters blank analysis confirmed that this temperature was enough high to drive off all determined compounds (Table 2.1). Therefore blank filter contamination does not affect sampled filter results.

To determine ambient concentration of PM_{10}, the European Standard EN 12341 recommends the initial and final weighing of filters (average of three measurements), after having conditioned them for 48 h in a temperature- and humidity-controlled chamber (20°C < T < 25°C, Relative Humidity = 50 ± 5). The collected particulate will be extracted to determine the concentration of PAHs, which degrade easily; furthermore both light and high temperature aid this process[23]. For this reason, the sampled filters, after being placed in petri dishes, were packed with aluminum foil and the weighing was conducted after conditioning them only for 20 h. Then they were stored in a refrigerator (3°C) until PAHs determination.

2.1.4 Particulate PAHs analysis

In this study the 4, 5, 6 rings compounds of the US EPA PAHs priority pollutant list were determined (Table 2.1), because they are mainly adsorbed on airborne particulate matter. Filters were extracted three times with 10 ml of a 7:3 v/v cyclohexane (Sigma Aldrich, HPLC grade, >99.7%) acetone (Sigma Aldrich, HPLC grade, >99.8%) mixture in an ultrasonic bath, the first time for 30 min and the others for 10 min, at room temperature. The extract was then filtered by regenerated cellulose filters (Econofilter 0.20 µm, 25 mm, Agilent Technologies) and concentrated by rotary evaporator. Lastly, volume was adjusted to 1 ml with acetonitrile (BHD Prolabo, HPLC grade, >99.9%).

PAHs were determined by HPLC with a fluorimetric detector (Agilent 1200 Series). They were separated on a reverse phase column, 4.6 mm x 150 mm, 3.5 µm, Agilent ZORBAX Eclipse PAH. The elution program consisted of an initial water and acetonitrile mixture (v/v: 50/50%) which was maintained for 2 min, followed by a 20 min gradient to 100% acetonitrile. The eluent was then held at 100% acetonitrile for 6 min. The separation was performed with a constant flow rate of 1.5 ml/min at 25°C. Different species were identified and measured by the external standard method (Ultra Scientific). Excitation (λex) and emission wavelengths (λem) of the different species are reported in Table 2.1.

The PAH recoveries ranged from 74% to 85%, based on spiked recoveries for a PAH mixture (mean values for three tests). The main aim of this study is the comparison between coincident samplings; therefore the precision of the technique was considered the most important parameter to assess. A sampled filter has been divided into quarters; they have been weighed and extracted separately. The precision is always higher than 90%, with an average of 94%.

Table 2.1: PAHs concentration in blank filters; minimum and mean concentration values in sampled filters; programmed excitation and emission wavelengths used in fluorescence analysis for each PAH

PAH	Code	Mean concentration of blank filters (µg/l)	Minimum concentration values for samples (µg/l)	Mean concentration values for samples (µg/l)	λex	λem
Fluoranthene	Flu	0.22	1.54	9.43	235	460
Pyrene	Pir	0.27	1.91	11.39	235	390
Benz[a]anthracene	B(a)A	0.28	0.54	6.27	270	410
Chrysene	Cri	0.45	0.95	11.11	270	410
Benzo[b]fluoranthene	B(b)F	0.055	0.87	20.72	270	410
Benzo[k]fluoranthene	B(k)F	0.093	0.39	7.73	270	410
Benzo[a]pyrene	B(a)P	0.020	0.64	12.50	270	410
Dibenz[a,h]anthracene	D(a,h)A	0.11	0.50	7.66	270	415
Benzo[ghi]perylene	B(g,h,i)P	0.017	0.83	13.31	270	415
Indeno[1,2,3-cd]pyrene	I(1,2,3)P	0.080	0.87	19.42	250	490

2.2 RESULTS AND DISCUSSION

2.2.1 PM_{10} air concentration

PM_{10} air concentrations (Table 2.2) show typical values of a medium polluted suburban area[24,25,26]. In the spring, the PM_{10} air concentration is always lower than 19 µg/m^3, while in the autumn, values of particulate matter concentration range from 9.1 µg/m^3 to 67.7 µg/m^3. Seasonal variation must be partially ascribed to the different mixing layer height: lower during the autumn, it varies from 110 m to 370 m, and greater in the spring, when it is over 400 m. In Table 2.2 meteorological parameters are also reported. From the data, it

can be inferred that the study area is generally characterized by low speed winds, i.e. light and gentle breeze; during no sampling, winds reach moderate breeze speed (> 5.5 m/s).

By comparing PM_{10} concentration in the air masses coming from the inland (C1) and from the coast (C2), differences below 10% are observed for 3m, 5m, 10w, and 11m samples. These samplings coincide with more instable weather conditions i.e., higher wind speed, about 3 m/s or more, and heavy rain. These conditions led to a greater atmospheric mixing, which tends to cancel the differences between the two air masses. 4w, 6w and 12w samplings are some exceptions. However, for 4w sampling, the particulate concentrations are very low; so, even if the relative difference between the two concentrations is quite high, the absolute difference is low. On the other hand, 6w and 12w samples show similar PM_{10} concentration, even if they were collected on stable weather days.

PM_{10} concentration in air masses coming from the coast is usually greater. No particular trend capable of distinguishing midweek samples from weekend ones has been registered.

Table 2.2:PM_{10} air concentration and meteorological parameters during the autumn and spring sampling campaigns.

		Concentration of PM_{10} C1 ($\mu g/Nm^3$)	Concentration of PM_{10} C2 ($\mu g/Nm^3$)	Mixing-H (m)[a]	Wind speed (m/s)[b]	Rainfall (mm)[b]	Temperature (°C)[c]	Visible radiation (W/m^2)[b]
FALL	1m	57.7	67.7	260	2.36	0	13.16	124.139
	2w	44.6	26.2	210	2.46	0.2	9.33	107.194
	3m	14.2	15.0	370	4.48	8.6	9.38	43.262
	4w	12.5	9.1	350	3.27	13.6	10.42	75.231
	5m	19.7	20.6	310	3.26	19.6	9.55	83.193
	6w	54.9	54.4	160	1.79	0.2	10.16	56.312
	7m	29.2	46.4	110	0.89	1.6	10.61	38.205
	8w	36.9	47.2	170	1.64	0.2	10.48	37.120
	9m	32.2	41.7	140	1.54	0.4	9.39	33.928
	10w	18.2	20.3	260	3.59	6	11.55	58.526
	Average	32.0	34.8	230	2.53	5.0	10.4	65.7
SPRING	11m	18.1	18.7	410	2.90	7.8	15.11	211.693
	12w	12.3	13.7	430	2.14	0	16.42	245.453
	13m	14.4	17.8	500	2.60	1.6	18.29	232.959
	14w	9.2	13.5	410	2.30	0	18.55	311.324
	15m	11.7	15.8	440	2.39	19.8	22.9	261.635
	16w	11.7	14.6	450	2.26	19.4	18.87	189.967
	Average	12.9	15.7	440	2.43	8.1	18.4	242.2

[a]Valuesprovided by Arpa Emilia Romagna Servizio IdroMeteoClima.They have been estimated by the model CALMET.

[b] Values provided by Arpa SIM (ServizioIdroMeteorologico) Emilia Romagna. Data obtained by real time measurements at a monitoring station 8 km far from the sampling site.

[c] Values registered by the PM_{10} medium volume sampler.

2.2.2 PAHs

Particulate PAHs air concentrations are reported in Figure 2.2. Autumn period values are one order of magnitude greater than spring period ones, in accordance with the results reported by other studies; PAHs in cold seasons are generally higher by a factor of 1.5 to 10 than those in warm seasons[27,28,29,30]. This is due to several reasons. As for PM_{10} air concentration, lower mixing layer height leads to increased PAHs concentration. Nevertheless, the mixing effect contributes only for about one third of the total, as can be

inferred from the PM_{10} concentration variation. Therefore there are other factors that lead to a decrease in concentration. Quantitatively, the most important process for the degradation of PAH in the atmospheric environment is photochemical oxidation. These reactions are dependent on the intensity of received solar radiation and thus are expected to have a greater effect during the spring months, when there is a higher number of daylight hours and an increase in solar intensity[31,32] (Table 2.2). An important effect is due to the decrease in temperature in the autumn period. This leads PAHs to be adsorbed on particulate matter, rather than remain in the vapor phase. For the same reason, the first sampling campaign is characterized by higher PAHs emissions, due to domestic heating.

In the autumn period, PAHs concentrations in air masses coming from the inland (C1) and from the coast (C2) show differences lower than 10% for 3m, 4w, and 5m samples. The coincidence with atmospheric instability is still greater than for PM_{10} concentration. In this case, 10w sampling is an exception. The difference between the air masses is quite high, even if the meteorological conditions were unstable. On these days, the mixing layer was on the average 260 m high, while during the 3m, 4w and 5m samplings it was more than 300 m high. Thus, this parameter also affects mixing conditions.

In the spring period, the differences between the two air masses are usually lower. This is combined with a very high mixing layer height, as reported above. For 12w and 16w samples, the difference between the concentrations in the two air masses is greater than 10%. On these days, wind speed was lower. The residual standard deviation (RSD) of PAH concentrations in the two air masses has been determined for each sampling. Pearson's product moment correlation analysis has been applied in order to evaluate the relationship between the above mentioned RSD and meteorological parameters (Table 2.3). The results confirm that an higher mixing layer height and a faster wind speed lead to a greater atmospheric mixing, which determines the disappearance of possible differences between the two air masses. The effect of the rain is lower. However, by considering only autumn samples, the effect of this parameter increases ($r=-0.67$, $p=0.03$).

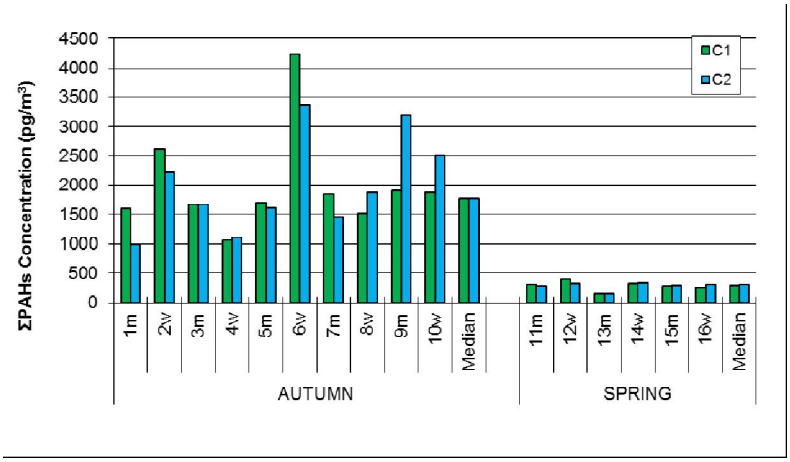

Figure 2.2: Total particulate PAHs air concentrations (pg/m^3)

Table 2.3: Results of Pearson's product moment correlation analysis between RSD of PAH concentrations in the air masses and meteorological parameters

	Temperature (°C)	Rainfall (mm)	Mixing-H (m)	Visible radiation (W/m^2)	Wind speed (m/s)
RSD (all samples)	-0.24 p=0.37	-0.42 p=0.11	-0.58 p=0.02	-0.36 p=0.17	-0.50 p=0.05

Distribution profiles for each sample are reported in Figures 2.3 (autumn period) and 2.4 (spring period). They are usually similar in the two air masses. For the autumn period, not only do the 3m, 4w and 5m samples have similar total PAHs concentration in the two air masses, but the congener profiles are almost the same also. This is also true for 2w samples. Other autumn samples show greater differences. For the 1m, 6w, and 7m samples, PAHs concentration is greater in air masses coming from the inland. Four-ring compounds (Flu, Pir, B(a)A and Cri) have similar concentrations, while differences are greater for five- and six-ring compounds. The latter are vehicular traffic markers[33], so their higher concentration may be due to the contribution of the motorway. For the other samples, the total PAHs concentration is greater in the air masses coming from the coast and every congener shows this trend. Particular differences which could distinguish midweek samples from weekend ones have not been registered.

For the spring period, 11m, 13m, and 15 samples show very similar profiles in the two air masses. For 12w samples, the concentration of five- and six-ring compounds is greater in the air masses coming from the inland, while for 16w samples, Flu concentration is

greater in air masses coming from the coast. For 14w samples, even if total PAHs concentration is very similar in the two air masses, the profiles are different. Four-ring compound concentration is greater in air masses coming from the inland, while the concentrations of five- and six-ring compounds are greater in air masses coming from the coast. Wind speed on these days is one of the lowest observed. Only during 12w and 16w samplings is the wind speed lower.

Comparing the two sampling campaigns, considerable differences can be observed. The profile of autumn samples is very similar to what is typically registered in urban areas, where the main PAHs source is vehicular traffic[16,34,35]. In the spring, distribution profiles are rather different; in particular, relative Flu and Pir concentrations are greater. This happens especially during two samplings (15m and 16w), when the concentration of these compounds accounts for more than 50% of the total mixture.

Considering the concentration of single PAHs in the particulate, Flu is the only one that shows similar concentrations during the two campaigns, i.e. 5 mg/kg in the spring and 4 mg/kg in the autumn for C1 samples, and 4 mg/kg in the spring and 5 mg/kg in the autumn for C2 samples, even if the higher temperature should prevent its condensation on the particulate.

Since in the spring there is a high Flu and Pir contribution on some days, their high concentration seems due to the effect of a specific source. This is confirmed by the comparison of the percentage contribution of each compound to the PAHs mixture; if Flu and Pir are not included, no differences between the two campaigns are observed.

Concentration profiles suggest that in the spring there is an additional source of Flu. It is not easy to understand what it is, since this compound is a fingerprint of several emission sources[36].

The sampling site is located in a suburban area, near various farmlands. Especially in the spring, the open-air burning of agricultural debris and weeds is common. Flu and Pir are the compounds most emitted from this combustion process[37,38,39].

With regard to MSWIs, few studies report Flu and Pir concentration in the emission stack, since they are not included by the 2000/76/EC directive among the compounds to be analyzed in incinerator emissions. However, a study by ARPA[40] reported that Flu is, among the PAHs, the compound with the highest concentration in the incinerator

emissions, both in the gas phase and in $PM_{2.5}$. Furthermore, an environmental monitoring close to a MSWI reports high concentrations of Flu and especially of Pir[41]. These studies would thus suggest that Flu and Pir might also be considered waste incinerator markers. But the higher concentration of these compounds only in the spring period is difficult to explain. In addition to this, when PAHs concentration is higher in the air masses coming from the inland, this is due to a higher concentration of five- and six-ring compounds, while four-ring compounds show similar concentrations. Finally, since both air masses show a high Flu concentration, the additional source is not likely a point one.

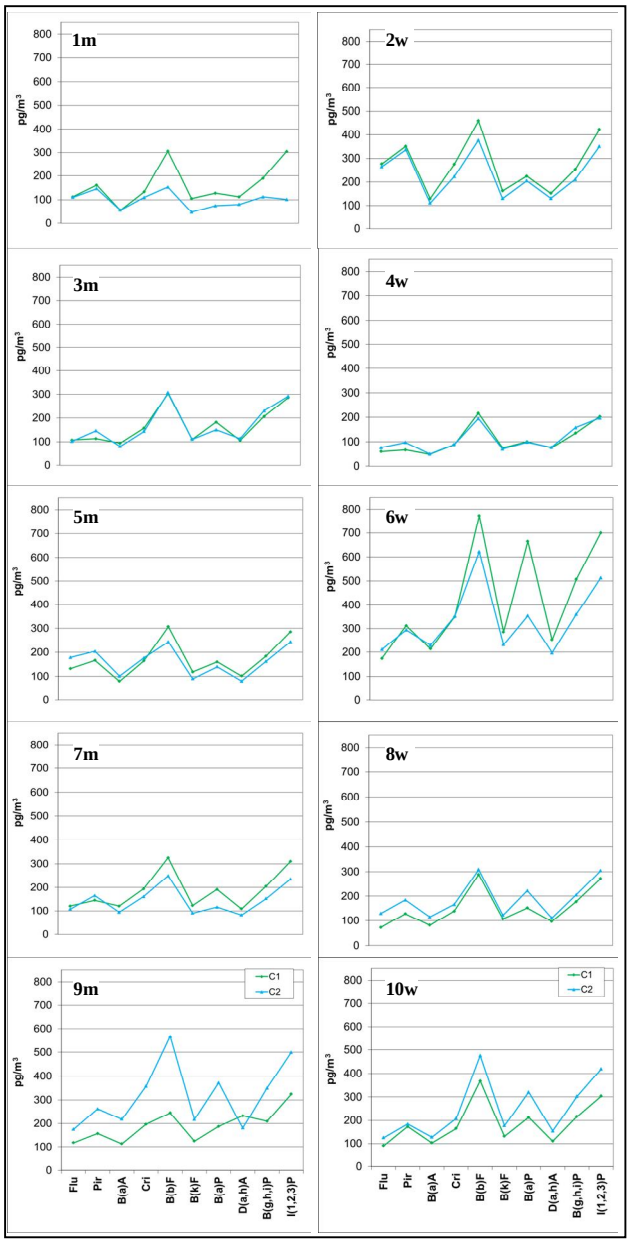

Figure 2.3:Distribution profiles of PAHs for each sample during autumn campaign

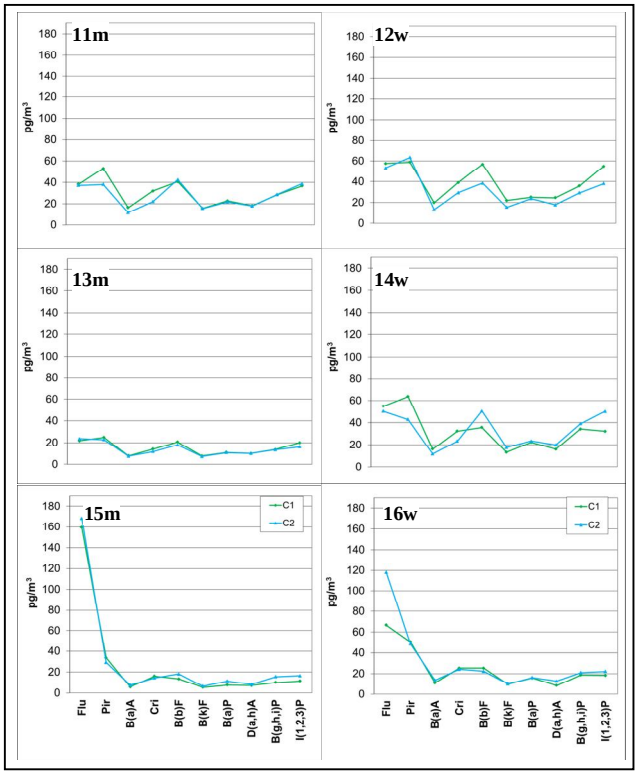

Figure 2.4:Distribution profiles of PAHs for each sample during spring campaign

2.3 CONCLUSION

The sampling technique, based on two PM samplers coupled with a wind select sensor, may be a valid support in source apportionment studies. However, meteorological and territorial conditions could strongly affect the results. The technique is suitable for areas characterized by moderate winds and with two prevailing directions, as in the case of costal zones.

The two sampled air masses monitored in this study often proved very similar, as far as the analyzed compounds are concerned. The study area does generally not seem characterized by a dominant source, but by a widespread contamination due especially to vehicular traffic. On some days, the biomass burning of agriculture debris seems to contribute in a not negligible way. Even though the incinerator is an emission source, one which commonly creates concern in the public opinion, in this case a remarkable effect has not been observed.

Because of the lower mixing layer height that limits the pollutant dispersion, the differences between the two air masses are greater in the autumn.

In order to further analyze the contributions made by the different emission sources,the inclusion of other chemical fingerprints seemed necessary. Therefore another sampling campaign was undertaken and new specific markers have been investigated in different PM fractions, in order to obtain more complete and quantitative information on the sources affecting the area.

3 Biomass combustion contribution on atmospheric particulate chemical composition

3.1 EXPERIMENTAL METHODS

3.1.1 Sampling

The sampling site is the same described in chapter 2.1.1. The sampling campaign of TSP and of the subfractions PM_{10} and $PM_{2.5}$, started on the 9th of March and finished on the 8th of April, 2011. Each sampling lasted 48 hours. Overall, 39 samples were collected, 13 for each fraction.

Two medium volume samplers (Skypost PM, TCR TECORA), one equipped with a PM_{10} sampling head, the other with a $PM_{2.5}$ sampling head were used. Each sampler operated at the flow rate of 38.33 l/min. In addition to these, a third sampler, (ECHO HiVol, TCR TECORA), operating at the flow rate of 200 l/min, has been used for the collection of TSP.

3.1.2 Analysis

$PM_{2.5}$ and PM_{10} samples were collected on 47 mm quartz fiber filters, TSP on 102 mm quartz fiber filters (MUNKTELL). Details on the determination of ambient concentration of PM_{10} and $PM_{2.5}$ are reported in chapter 2.1.3. After PM quantification, each filter was split in parts for the different chemical specie determination (Figure 3.1):

1/4: OC and EC (1 cm^2 filter punch), the remaining part for ions

1/8: levoglucosan (Lvg)

3/8: polycyclic aromatic hydrocarbons

1/4: metals

The subsamples dimensions were chosen on the basis of expected air concentration of the different chemical speciesand of the instrumental limits of quantifications.

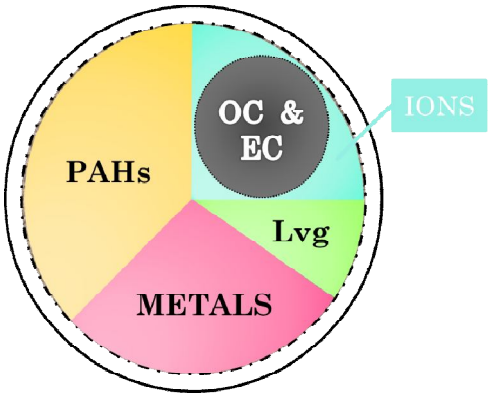

Figure 3.1:Filter split for the different analysis

For the determination of inorganic ions, the filters were extracted with 5 ml of bidistilled water for $PM_{2.5}$ and PM_{10} and with 20 ml for TSP, in an ultrasonic bath for 40 min at room temperature. The obtained solution is filtered with inorganic membrane filters with pore size 0.2 μm (Anotop 10 IC, 0.2 μm 10 mm, Whatman) and the ions (SO_4^{2-}, NO_3^-, Cl^-, Ca^{2+}, Na^+, NH_4^+, Mg^{2+} and K^+)were determined by ionic chromatography couplet with a conductibility detector (Metrohom, 761 Compact IC). Cations were separated on a Metrosep C2/150 column (150 x 4 mm), with a isocratic elution (Dipicolinic acid (Sigma Aldrich) 4 mM, tartaric acid (Sigma Aldrich) 1mM) and a flow rate of 1.5 ml/min. Anions were separated on a Metrosep A supp 4 column (250 x 4 mm), followed by a suppressor, with a isocratic elution ($NaHCO_3$ (>99.8% Carlo ErbaReagenti) 1.7 mM, Na_2CO_3 (anhydrous, >99.5%, Carlo ErbaReagenti) 1.8mM and acetone 2% (Sigma Aldrich, HPLC grade, >99.8%)) and a flow rate of 1.5 ml/min.

Each ion was quantified by external standard method (Ultra Scientific).

The Thermal Optical Transmittance (TOT) technique by the Sunset Carbon Analyzer Instrument has been used to determine elemental carbon (EC) and organic carbon (OC) mass concentrations. From the mathematical elaboration of the carbon dioxide release curves, it has been possible to obtain also the carbonate carbon concentration[42].

Also in this study, 4, 5, 6 rings compounds of US EPA PAHs priority pollutants (Table 2.1) were determined. They were determined with the same procedure reported in chapter 2.1.4. The only difference with the previous procedure was that PAHs were quantified by internalstandard method. Therefore before the first extraction, the sampled filter was

spiked with 50 µl of internal standard 6-metyl-chrysene 1 mg/l (Absolute Standards, Inc.), as suggested by ISO 16362 method.

Lvg extraction procedure is based on the method proposed by Fabbri et al[43]. The filters of $PM_{2.5}$ and PM_{10} were extracted for 30 min with 15 ml CH_3OH (HPLC grade, >99.9% Sigma Aldrich) under ultrasonic agitation in 20 ml screw neck vials. For TSP a second extraction with 10 ml CH_3OH for 20 minutes was necessary, since the amount of particulate was greater. The extracts were filtered with a 5 ml syringe through a 0.22 µm nylon filter (Cameo 25NS, STEFBIO) and dried by rotary evaporation. The residue was re-dissolved with 0.5 ml CH_3CN added with 20 µl pyridine (Anhydrous pyridine, 0,0075% H_2O maximum, >99,5%, Carlo ErbaReagenti) and 100 µlbis(trimethylsilyl)trifluoroacetamide (BSTFA, Merck KGaA) containing 1% trimethylchlorosilane (TMCS, Carlo ErbaReagenti) and transferred into 1 ml glass flask. The silanization reaction was conducted at 60°C for 2 h. After the solution had cooled down, the volume was adjusted to 1 ml.

The extracts were analyzed by GC-MS (Shimadzu 3400 GCMS-QP2010 Series). Separation was performed with a RESTEK Rtx®-5MS column (95% dimethyl- 5% diphenylpolysiloxane, 30 m, 0.25 mm i.d., 0.25 µm film thickness) with a temperature programme from 100°C to 200°C at 10°C/min and from 200°C to 300°C at 50°C/min, with helium as carrier gas (purity: 100%). The AOC – 20i, Auto-Inject split/splitless injector was maintained at 260°C and operated under split conditions. Data acquisition was performed in the sim mode at 204 and 217 m/z, the characteristic masses of the fragment ions of Lvg. Lvg was identified and measured by the external standard method, using solutions of persilylatedLvg (Merck Schuchardt OHG, for synthesis, 1 g) with different concentrations.

Metals (Al, Cd, Cu, Ni, Pb) were determined after mineralization of filters in a Multiwave 3000 (Anton Paar) microwave oven, according to UNI-EN 14902 method. The obtained solutions were analyzed with the Perkin Elmer AAnalyst 400 Atomic Absorption Spectrometer (AAS) equipped with electro-thermal (graphite tube) and flame atomizers. Standard solutions were prepared daily in 0.2%HNO_3, by serial dilutions of stock standard solutions (Carlo ErbaReagenti and Merck kGaA).

3.1.3 Precision and recovery test

Trueness results reported in chapter 2.1.4 are based on spiked recoveries for a PAH mixture.To better investigate trueness of PAHs extraction, the NISTstandard reference material (SRM)1649b urban dust was purchased. The PAH recoveries ranged from 51% to 64%, with a standard deviation always lower than 2% (mean values for four tests). D(a,h)A is an exception; its recovery is 129±2%, so the compound clearly shows coelution. Several studies[44,45] report that D(a,h)A coelutes with dibenzo(a,c)anthracene, at least in GC-MS. For this reason dibenzo(a,c)anthracene standard (Ultra Scientific) was analyzed by HPLC, but its elution time is well different than D(a,h)A one. By analyzing the SRM in GC-MS, the coelution of D(a,h)A with another PAH of 278 molecular weight was clear, but it was not possible to recognize which compound was. Precision results for sampled filter are reported in chapter 2.1.4.

Lvg recovery was 81±6%, based on spiked recoveries for a Lvg standard (mean values for six tests). Extraction yield was considered satisfactory; therefore the surrogate standard has not been used. The precision of the technique for sampled filter was obtained in the same way as for PAHs, but this time the filter has been divided in six parts. The precision was 95%.

The precision for ions for sampled filter was always greater than 90%, with an average of 94%.

Metal recoveries ranged from 70% to 103%, with a standard deviation always lower than 6% (for aluminum it is quite higher, 15%). The results are based on the extraction of the NIST standard reference material (SRM), 1648 urban dust (mean values for four tests). The precision for sampled filter was always higher than 85%, with an average of 93%.

3.2 RESULTS AND DISCUSSION

3.2.1 Particulate matter size distribution

Airborne particulate concentrations are reported in Figure 3.2. Mean values are 25, 34 and 40 $\mu g/m^3$ for $PM_{2.5}$, PM_{10} and TSP, respectively. Even if these data represent a short period, in comparison with the limit reported in 2008/50/CE directive, atmospheric particulate concentration in the city of Riccione is not particularly high.

The comparison between particulate concentrations and meteorological data shows that during the days characterized by heavy or moderate rain and moderate or however higher than 4 m/s wind, the particulate concentration in atmosphere decreases. By considering the decreasing concentration trend, there is an inverse relationship with the temperature. This typical correlation is probably due to an increase in the mixing layer height, which leads to a greater pollutants dispersion, as deeply discussed in chapter 2.2. The maximum particulate concentration is registered on 18th-20th March, when "fogheracce" have been ignited (18th of March).

In March the particulate size is mainly fine. The fraction $PM_{2.5}$ represents on the average the 66% of the TSP, whereas the coarse fraction is the 20%. During the last two samplings of the campaign, which were undertaken on April, the granulometric distribution is different; the coarse fraction is the 42% of the TSP, while the fine fraction is only the 33%.

During the sampling of 18th-20th of March, the granulometric distribution is similar to the previous days.

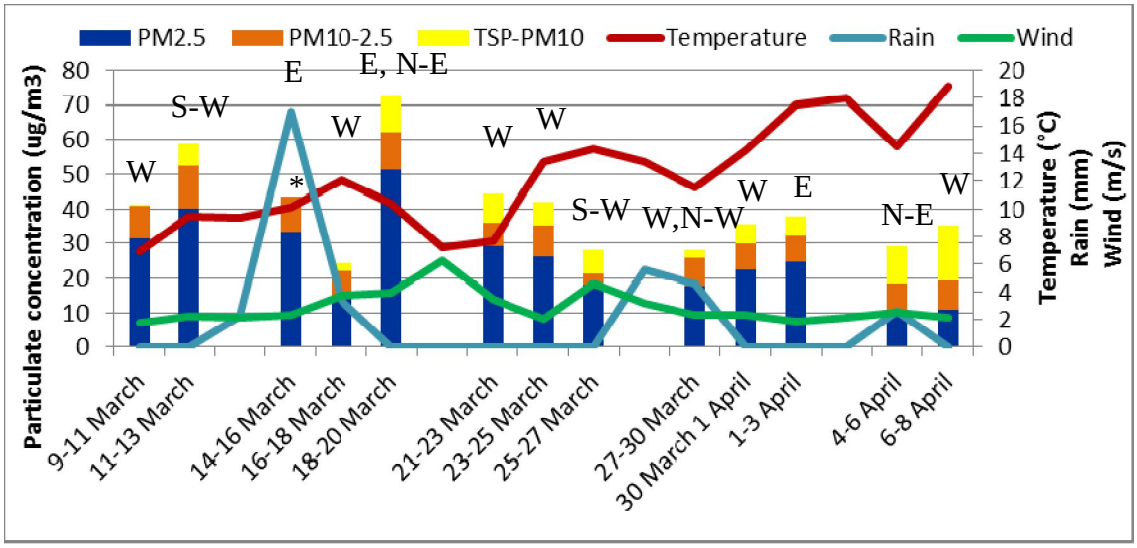

Figure 3.2: Particulate granulometric distribution and its relationship with meteorological parameters during the sampling campaign. E=east, S=south, W=west, N=north.

** TSP data on 14th-16t^{h} of March is not present because the sampler did not work*
$^{\#}$ meteorological data provided by a 8 km far monitoring station of the regional environmental protection agency Arpa -Emilia Romagna

3.2.2 Chemical characterisation

3.2.2.1 Soluble Ions

Figure 3.3 shows the concentration of soluble ions in the different fractions of particulate matter, and the median value.

As predictable, the most abundant soluble ions are nitrates, sulfates and ammonium (NH_4NO_3 and $(NH_4)_2SO_4$), mainly related to secondary particulate matter, as confirmed by the almost exclusive presence of these compounds in the fine fraction. The other fractions ($PM_{10\text{-}2.5}$ and TSP-PM_{10}) are mainly composed by calcium, magnesium and carbonates related to re-suspended soil dust, and by sodium and chlorine, related to marine spray. Sulfates due to marine spray contribution are less than the 10% of the total.

The granulometric distribution of soluble ions during each sampling is quite changeable, especially for chemical species due to primary sources such as sodium, chlorine, calcium and carbonates.

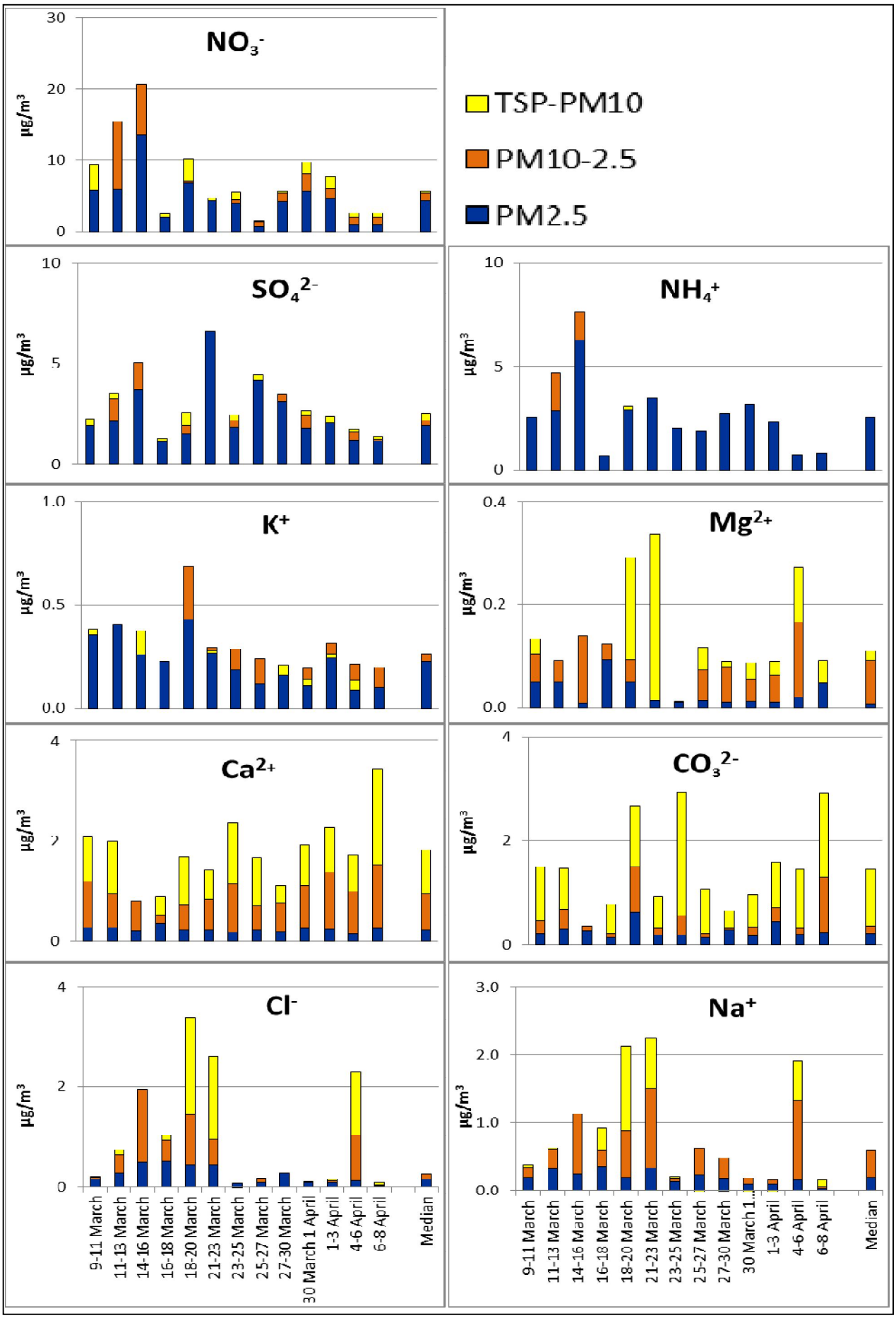

Figure 3.3: Granulometric distribution of soluble ions.

During Saint Joseph bonfires, in comparison with other samples, potassium concentration increases by 100% in fine fraction and by 250% in coarse fraction. In the same samples, NO_3^-, NH_4^+, SO_4^{2-}, Mg^{2+}, Ca^{2+} and CO_3^{2-} also increased. This ion could be directly or indirectly ascribed to combustion ash.

Since during these days the prevalent wind direction was sea breeze,the higher concentration of Cl^-, $Na^+$and Mg^{++} could not be ascribe only to biomass burning,

3.2.2.2 Elemental and Organic Carbon

The mean concentrations of OC are 3.5 µg/m^3 for $PM_{2.5}$ and PM_{10} and 4.7 µg/m^3 for TSP, while the mean concentrations of EC are 0.4 µg/m^3 for $PM_{2.5}$, 0.6 µg/m^3 for PM_{10} and 0.7 for TSP. These values are similar to what is generally found in suburban areas in Europe and much lower than what is found in urban areas[42,46,47].

OC represents 14%, 10% and 12% of particulate for $PM_{2.5}$, PM_{10} and TSP, respectively. EC contribution to the total mass of particulate is strongly lower: 1.4% for $PM_{2.5}$ and 1.8% for PM_{10} and TSP. The distribution of OC and EC in the different fractions is different. OC is present on the average for the 75% in $PM_{2.5}$ and for the 24% in TSP-PM_{10}, whereas EC is present for the 49% in the fine fraction, for the 33% in the coarse fraction and for the 18% of the ultra-coarse fraction. The different granulometric distribution is coherent with their principal formation processes: EC is essentially a primary pollutant, mainly emitted by combustion processes, and in the coarse fraction might also come from tire debris or soot deposited on re-suspended dust[17,48]. OC, instead, consists of primary and secondary species from anthropogenic and biogenic origin; for this reason it is principally present in the fine fraction. Coarse OC may also include biological debris[17,48], in addition to construction, agriculture, and natural soil contribution[49].

OC/EC ratio is strongly influenced by the geographical area. In urban and rural areas this ratio is much lower than what is measured in an ambient air sample collected at a remote area, (South Atlantic Ocean = 160[50]) where the influence of both petroleum combustion and biomass burning emissions is negligible[39]. Thus, the low OC/EC ratios for many urban and suburban areas indicate a strong influence of petroleum derived combustion emissions.

In this study OC/EC ratio decreases during the sampling period, due to the lower presence of biomass combustion processes in the spring period.

3.2.2.3 Levoglucosan

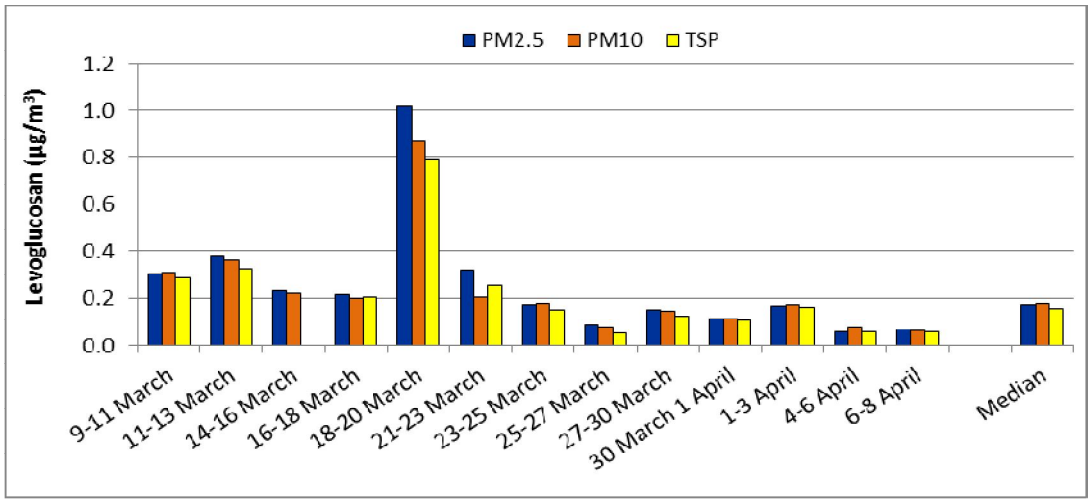

Figure 3.4:Lvg concentration in the particulate fractions

Median concentrations of Lvg (Figure 3.4) at the sampling site are similar to winter data of other European towns[43,51,52,53,54]. As well as reported in the literature, Lvg concentration decreases when the temperature increases due to both the reduction of biomass use for heating and the higher atmospheric mixing layer.

Lvg is present almost exclusively in the fine fraction. Some data series show a greater concentration of Lvg in $PM_{2.5}$, rather than in TSP and PM_{10}. Therefore it is probable that the coarse fraction, someway, degrades or creates artefacts during the sampling, or it can interfere during the extraction. Even if it is not very clear what causes these lower analytical yields, by the study of mass spectrum of chromatograms peeks, it was possible to exclude interference effects due to sample silanization.

On 18th-20th March, in comparison with the sampling period average, Lvg concentration increase of 500%.

In PM_{10},the mean contribution of Lvg to OC is 2.7%, while K/Lvg ratio is 1.2, similar to what is found in winter in other areas subjected to wood smoke emissions[54]. Among the possible sources of Lvg, others than outdoor biomass combustion or household heating, the MSW incinerator was also taken into consideration. Indeed, cellulose represents a

great part of municipal solid waste, which is composed by about 25% of paper. In order to verify the MSWI emissions, two PM samples were collected at the stack of the plant. In both the samples the Lvg concentration was under the instrumental limit of detection. This means that Lvg concentration was< 2 ng/m^3 for the first sample and < 5 ng/m^3 for the second one. For this reason the contribution of the incinerator to Lvg air concentration was considered negligible

3.2.2.4 PAHs

Since the use of high volume sampler provided a greater quantity of particulate, PAHs were determined only in TSP samples. Laboratory tests have confirmed that PAHs are completely present in $PM_{2.5}$.For 14th-16th, $PM_{2.5}$ was analysed.

On 18th ofMarch, PAHs concentration increases, by 900% by considering the previous sampling and by 650% by considering the mean value of the campaign. In addition to this, the profile of these compounds during this sampling is different compared to the other samplings (Figure 3.5). The profile usually found is typical of urban areas, where the main source of PAHs is vehicular traffic[16,34,35]. On 18th of March instead the concentration of each compound increases, especially Cri, while Flu and Pir, the PAHs generally related to biomass combustion[37,38,39], have a concentration similar to other days. The different profile could indicate a different origin of PAHs in atmosphere.

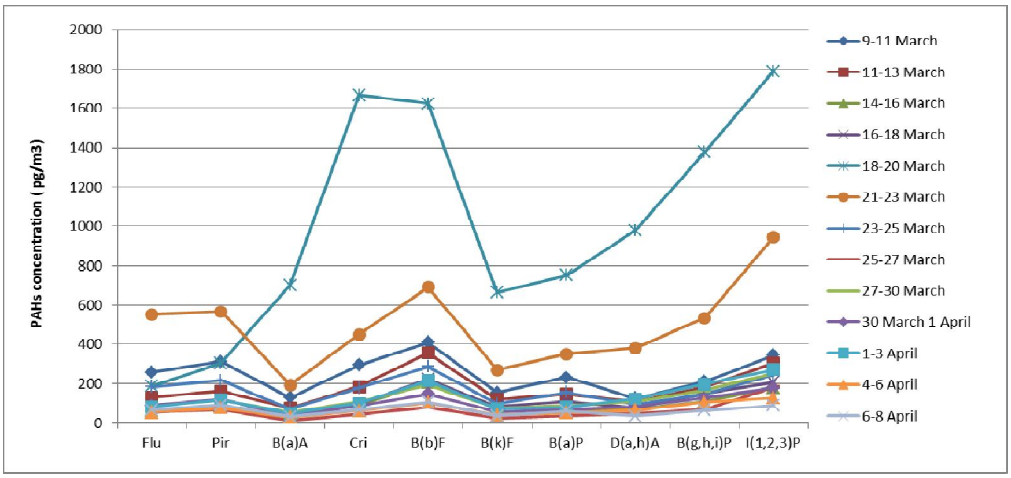

Figure 3.5: Distribution profile of PAHs for each sample

The usefulness of ratio-ratio plots as visualization tools for particle bound PAHs has been demonstrated by Robinson et al.[55] and successfully applied in other studies[56,57,58]. With

this technique scatter plots are constructed with data for three species – two target compounds whose concentration are normalized by the same reference compound, by which the mixing of more sources are considered. The advantage over diagnostic ratios and simple scatter plots is that ratio-ratio plots visualise a portion of the solution space for indication of inconsistencies between the ambient air data and source profiles. In this study plot data on B(g,h,i)P, I(1,2,3)P and EC were used to visualize a hypothetical four source scenario. It is evident in Figure 3.6 that most of the ambient PM samples place themselveson the Biomass/diesel axis. 6-8 April sample fall towards diesel-exhaust. Thus when temperature increases (this is the last sample of the campaign), biomass contribution decreases. Samples collected on "Fogheracce days" definitely distinguish themselves from the other. Gasoline seems also to play a role. However in this study only a characteristic ratio for biomass burning was used. More ratios can be found in the lieterature, depending on the nature of the biomass[56]. "Fogheracce" ratio represents bonfires, a particular kind of biomass burning and this ratio can be representative of a type of biomass different from the one reported in the study.

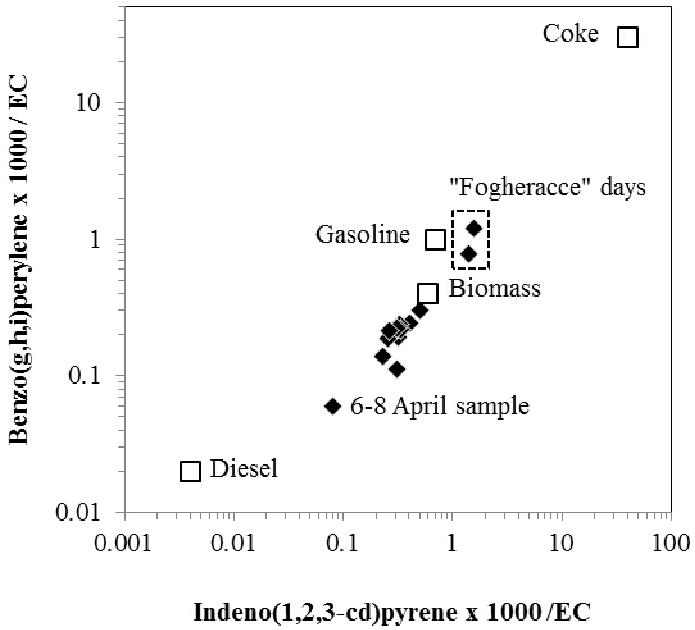

Figure 3.6:Ratio – ratio plot using data on B(g,h,i)P, I(1,2,3)P and EC to visualize the potential contribution of four source scenario for ambient PM.

3.2.2.5 Metals

Figure 3.7 shows the concentration of metals in the different fractions of particulate matter.

The 70% of Cu was detected in the coarse fraction, whereas only the 30% in the $PM_{2.5}$. Cu size distribution could be justified by tear brake and then principally related to the urban traffic emissions[59].

Ni and Cd were mainly enriched in the fine particle. Indeed, these elements could be ascribed to fossil fuel combustion[60,61,62,63,64].

The 70-90% of Al was detected in the coarse fraction, the 20% in the fine fraction, whereas the 10-30% in the TSP-PM_{10} fraction. As well as reported in the literature, Al in atmosphere has mainly a primary origin, due to resuspended soil dust[65].

On 18th-20th March Cd, Al and Pb concentrations are higher than on other days. Nevertheless Cd concentration is very changeable. Even if Cd concentration on 18th-20th March is three times higher than the mean value of the period, it is similar to what is registered on other days. Al concentration increases in all the study fractions, but especially in the fine fraction. By considering Al concentration in PM_{10}, the fine fraction represents the 80% on 18th-20th March, while the mean value of the period is lower than 40%. The stronger increment registered in the fine fraction demonstrates that biomass combustion is the additional source on these days. Al is one of the main constituents of soil, therefore it is abundantly present also in plants. Lead is the metal which increases the most when “fogheracce” have been ignited. Biomass combustion strongly contributes to atmospheric lead concentration.

The strong increase of these metals on 18th-20th March is due to their bioaccumulation by trees which grown on land contaminated by metals. Pyatt[66] reports that bioaccumulation and biomagnication of lead is particularly marked in Acacia and Eucalyptus. Alves[67] burned wood from seven species of trees to determine the chemical composition of fine particle emissions. From the 67 elements that have been searched for, 20 were typically found at quantifiable levels. By considering the metals analyzed in this study, only Pb and Al were always detectable in the smoke from all wood types.

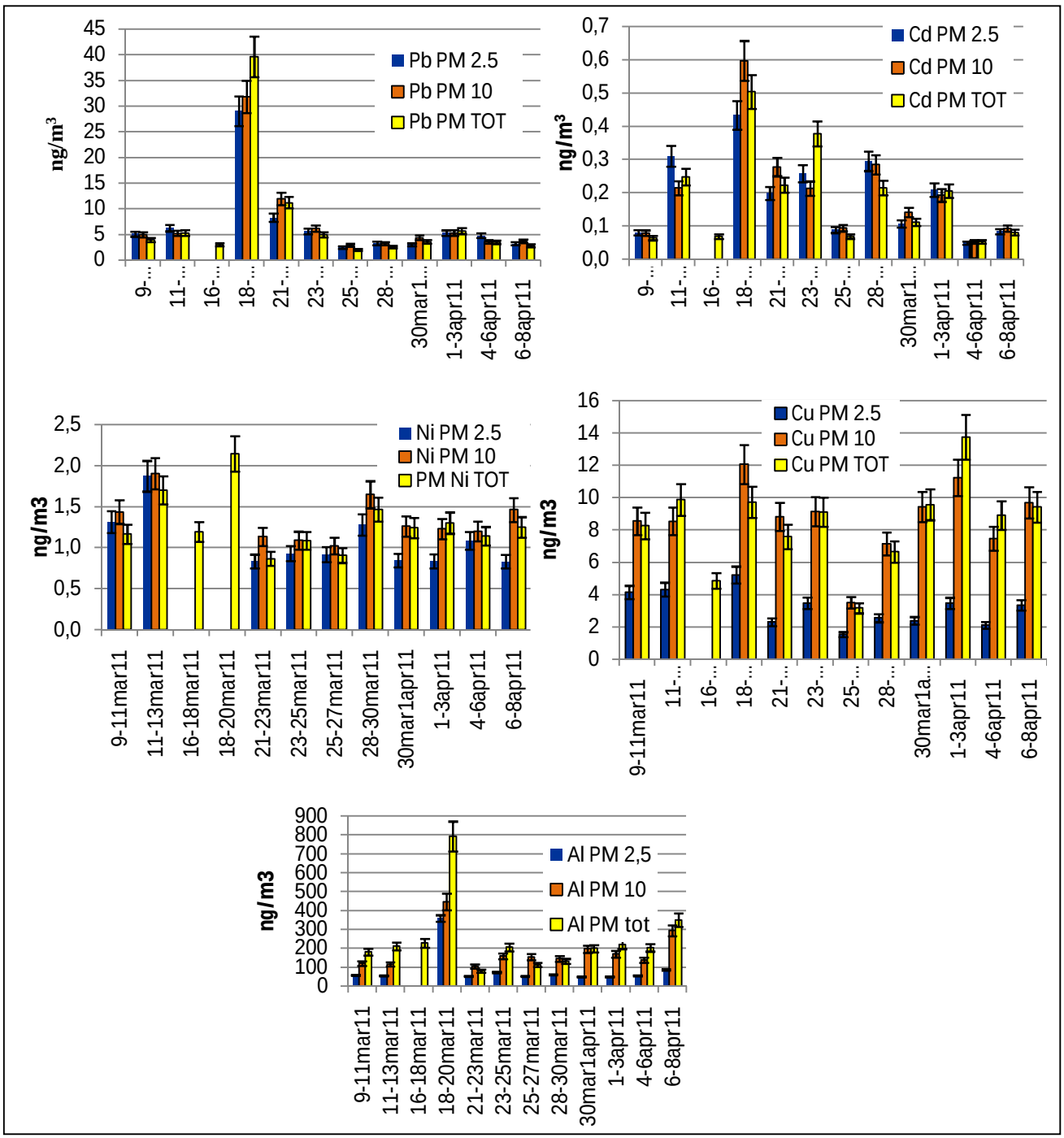

Figure 3.7: Temporal trend of metals

** Due to the insufficient amount of 16th-18th March $PM_{2.5}$ and PM_{10} samples, metals were not determined in these fractions.*

3.2.3 Enrichment factors

As above mentioned, the air concentration of many components of particulate matter increases when fogheracce are ignited, as far as the particulate matter concentration itself does. It is therefore important to assess how the particulate matter composition changes during this event. To do that, enrichment factors (EF) have been calculated (Figure 3.8):

$$EF(X) = \frac{([x]_{fog} / [PM]_{fog})}{(\overline{[x]} / \overline{[PM]})}$$

where

$[x]_{fog}$ = Concentration of compound x on 18th-20th March sample

$[PM]_{fog}$ = Concentration of PM on 18th-20th March sample

$\overline{[x]}$ = Mean concentration of compound x

$\overline{[PM]}$ = Mean concentration of PM

Potassium, which is a typical biomass combustion marker, is surprisingly not enriched in PM, only TSP is slightly enriched. Other combustion markers, i.e. OC and Lvg, are more enriched, especially Lvg, which confirms as a good marker of this type of combustion process. Al is also a good marker, especially in the fine fraction. But the compounds which are enriched the most are PAHs, exception for Flu and Pir, and lead. Open bonfires are a combustion process without any type of control; therefore the contribution of incomplete combustion products, such as PAHs, is particularly important. The high enrichment for lead is instead ascribable to its bioaccumulation in plants. In the past years anthropogenic emissions of lead were very high for its presence in gasoline. Nowadays this source is not present anymore but its past input can be still observed in plant bioaccumulation.

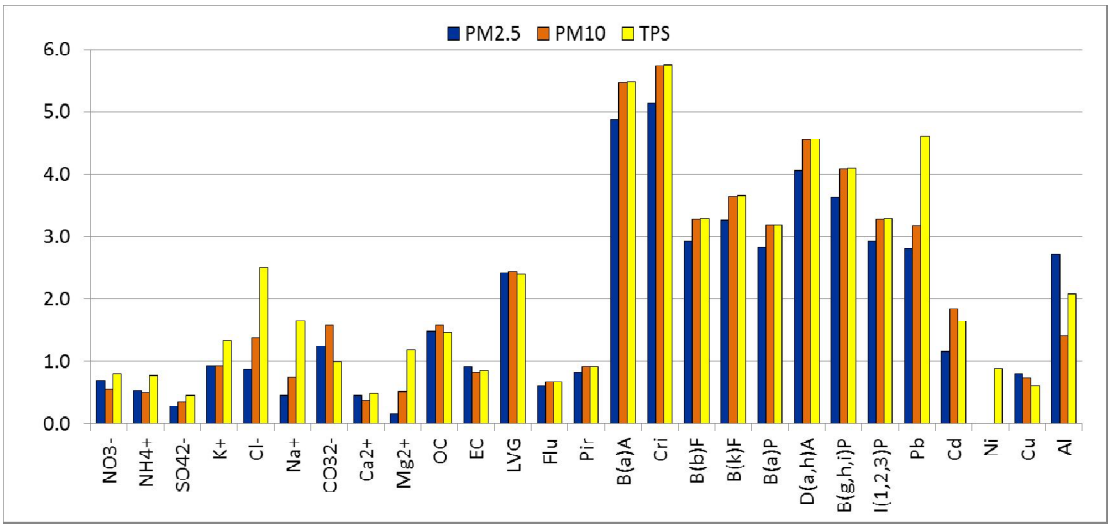

Figure 3.8: Enrichment factors for 18th-20thMarch sample

3.3 CONCLUSION

Granulometric fractions analysis of $PM_{2.5}$, PM_{10}-$PM_{2.5}$ and TSP-PM_{10} shows that they have very different composition due to the presence of several particulate sources in the study area. Fine particulate is rich of sulfates, nitrates, ammonium, potassium, cadmium, nickel, lead, elemental and organic carbon, thus PAHs and Lvg. It has an anthropic origin because these compounds are produced directly or indirectly from incomplete combustion processes. The coarse fraction is richer of carbonates, calcium, magnesium, sodium, chlorine and aluminium, so it is originated principally by natural sources, such as marine spray, crustal materials erosion and re-suspended soil dust.

Traditional "Fogheracce", ignited on Saint Joseph eve, are an important source of particulate and they lead concentration to increase especially for $PM_{2.5}$ and TSP. Ammonium and nitrates are found in the coarse and in the PM_{10}-TSP fractions, unlike what is reported in the literature and what is found in the other samples of the campaign. Therefore there is likely a contribution of combustion ash. Enrichment factorsprove that OC is a good biomass combustion process indicator. All organic compounds determined, i.e. Lvg and especially PAHs, are good indicator of this type combustion process. Among metals, lead and aluminium are well related to the biomass combustion event and could be considered representative biomass combustion indicators. Surprisingly, even if

potassium concentration is higher during bonfires event, PM is not enriched of this well-known combustion marker.

The Lvg background present in the environment has an inverse relationship with the temperature and can be ascribed to household heating. It has been demonstrated that the possible contribution of Lvg by the incineration plant, only 2 km far from the sampling site, is absolutely negligible.

This study has thus provided some useful information which could be used in future studies. On the basis of specific markers concentrations, it will be possible to estimate biomass combustion process contribution to particulate matter.

Since these results cannot give quantitative and complete responses on the causes of air pollution in the area, the implementation of data analysis with new and more powerful statistical tools was necessary to finally reach the aim.

Section II

Application of new statistical tools in data analysis

4 Chemometric methods of source apportionment and PMF analysis characteristics

4.1 RECEPTOR MODELS

Chemometric methods are very spread and useful in data analysis of complex dataset, since they allow to reduce the number of factors that explain a phenomenon and make the study easier to interpret. These methods are particularly important in environmental studies. They allow to colleague contaminants related to the same source and to undertake source apportionment studies. Application of chemometrics methods to the identification and quantitative apportionment of air pollutants to their sources is called receptor modeling. Typically, it employs methods of solving the mixture resolution problem using chemical composition data of the samples. In such cases, the outcome is the identification of the pollution source types and estimates of the contribution of each source type to the observed concentrations. It can also involve efforts to identify the locations of the sources through the use of ensembles of air parcel back trajectories[68].

There are several receptor models, depending on what information is available. If the number and nature of the sources are known, then the only unknown is the contribution of each source to each sample. Among these models, the most known and used is Chemical Mass Balance (CMB). This method has a big advantage: it can be applied even when only few samples are available. However a complete knowledge of emission inventories is necessary, it cannot have missing sources or missing data and it has some problems with markers which react in atmosphere. The methods to be used when the source profile are not known are forms of factorial analysis. They bypass the above mentioned CMB problems, they can help identify important missing sources and it is possible to use tracers that are somewhat reactive. However a large number of receptor samples is required, it is necessary to determine how many “factors” to retain and to evaluate which source is represented by each factor. Moreover a large number of solutions can be obtained, even with rotation and it is not possible to be sure that the optimal solution has been found. Positive Matrix factorization (PMF) is a new approach compared to Principal Component Analysis (PCA) and it has several advantages: as CMB, measure uncertainties and below detection limit data can be managed. Moreover missing data can

also be handled. But the most important characteristic is that loadings matrix has only positive values and this is a fundamental feature in source apportionment studies, where each factor should represent a different emission source[10].

4.2 POSITIVE MATRIX FACTORIZATION (PMF)

The two-dimensional Positive Matrix Factorization model (PMF2) for source apportionment assumes that there are p sources, source types or source regions (termed factors) impacting a receptor, and linear combinations of the impacts from the p factors to the observed concentrations of the various species[69]. Mathematically, the model is[70]

$$X = GF + E \quad (1)$$

where X(n x m) is the data matrix; n and m are the number of samples and species, respectively. G(n x p) is the contribution matrix where p is the number of source factors extracted. The first column shows how much pollutant from the first source was collected during each sampling, and so on. F(p x m) is the factor score matrix. Each column represents a single source of pollutants and the elements of the row show the mean concentrations of the compounds[71]. E(n x m) is the unexplained part of X, i.e. the residuals. The elements in G and F are constrained to non-negative values only. The objective of PMF analysis is to minimize the value of Q, which is defined as

$$Q = \sum_{i=1}^{n}\sum_{j=1}^{m}\left(\frac{e_{ij}}{s_{ig}}\right)^2 = \sum_{i=1}^{n}\sum_{j=1}^{m}(r_{ij})^2 \quad (2)$$

where e_{ij} are the elements in E and s_{ij} are the estimated standard deviations of the measured concentrations. The ratio between $e_{ij}$and s_{ij} (i.e. r_{ij}) represents the scaled residuals (R matrix). Each column in R represents the quality of fitting of each species to the product GF. Equation 2 is invariant with respect to scale changes. Thus the minimization problem of PMF does not change if the units used for any column of the matrix are changed; this will only effect the corresponding change of scale for the resulting factor concentrations[72]. This is an important feature, since one should avoid extremely large and extremely small values in the matrix[70].

PMF2 provides several options (error model, EM) to calculate the standard deviations (s_{ij}). The default is EM=-12 and it is based on the observed values. s_{ij} is computed once

before the iterative computation is started and it does not change during the iteration. According to error model -12, standard deviations are computed with the formula:

$$s_{ij} = C1 + C2\sqrt{|x_{ij}|} + C3|x_{ij}| \quad (3)$$

where C1, C2 e C3 are user-specified parameters. These parameters may be specified individually for each measurement, or globally for the whole matrix[73]. The second option is practical if all rows and columns of X represent the same physical quantity having the same error. The value C1 should be expressed in same units as the data values x_{ij}. C2 value is usually zero, except in Poisson-like situations, both if it is specified individually for each measurement, or globally for the whole matrix. C3 should be chosen so that the relative uncertainty of large values is reasonable; typically C3 is between 0.01 and 0.1.

Other error models compute S iteratively during the fit. EM -10 and -11 are used when data comes from a lognormal and a Poisson distribution, respectively. EM=-14 is recommended for general- purpose environmental work. Standard deviation is computed according to the formula[70]:

$$s_{ij} = C1 + C2\sqrt{\max(|x_{ij}|,|y_{ij}|)} + C3\max(|x_{ij}|,|y_{ij}|) \quad (4)$$

At the beginning, it is suggested to use the program with EM=-12. In order to deep the technique potentiality and therefore to try to improve results, other error models should be used.

The use of robust model has been suggested to analyze environmental data[70]. It can avoid excessively large values (outliers) in the data set, which can disproportionally affect the results[73]. When running in robust mode a measured value x_{ij} is processed as an outlier if

$$|x_{ij} - \Sigma_k g_{ik} f_{kj}| / s_{ij} > \alpha \quad (5)$$

in other words, if the scaled residual exceeds α times the standard deviation. The "processing as an outlier" means that the std-dev value s_{ij} is increased so that the "pull" or influence of the outlying value x_{ij} is no more than the pull of a value which is on the limit of being classified as an outlier. α= 2.0, 4.0, or 8.0 are suggested to be used as outlier threshold distance.

Some optional parameters are available with PMF2. "missingnegr" allows to handle missing values. It commands PMF to decrease the significance of all negative entries of the array X**.** This is realized so that PMF2 increases internally their std-dev values by the factor r and uses the value zero as the data value. With a suitable r=10...r=100 this may cause that these negative x_{ik} values have a negligible effect on the factors. "BDLneg r1 r2" combines missing data and below the detection limit data handling. If a data value x_{ij} is more negative than r1, it is treated as missing and its std-dev is increased internally by the factor r2. The value zero is used in the least squares fit, instead of x_{ij}. If, however, $r1<x_{ij}<0$, then it is assumed that $|x_{ij}|$ is the Detection Limit (DL) for a Below- Detection-Limit measurement. The corresponding std-dev value s_{ij} is computed normally but dynamic weighting is applied in order to achieve correct BDL handling[70].

There is rotational ambiguity in the results of all two-way factor analytic programs, including PMF2. The rotational state of the result by PMF2 may be controlled by commanding additions and subtractions of factors. This is similar to using the varimax technique. The "peaking parameter" is "FPEAK". By setting a positive value to FPEAK one forces the routine to search for such solutions where there are many (near-) zero values among the F factor values, and also many large (i.e. as large as allowed by the data) values, but few values of intermediate size. Technically speaking, a positive FPEAK forces the routine to try to subtract the F factors from each other (meaning that the G factors are added to each other). Correspondingly, FPEAK < 0.0 generates "peaks" on the G side. A negative FPEAK causes factors to be subtracted from each other on the G side. Good first trial values are between 0.1 and 1. "rotmat" is an output matrix which indicates the rotational uncertainty. It is a p x p matrix of standard deviations of rotational coefficients; it is one of the basis for estimating the uniqueness and accuracy of the computed factor values. Small elements of rotmat indicate a locked rotation. On the other hand, when the rotmat elements increase, the rotation is free and factor values are non-unique. If all elements in the i^{th} row of rotmat are "small", then one knows that the i^{th} G factor is uniquely determined without "any" rotational uncertainty. Similarly, a column of small elements in rotmat indicates a uniquely determined F factor[70].

An important parameter resulting from the PMF analysis is the explained variation (EV) value; it is dimensionless, it summarizes how important each factor element is in explaining one row or column of the observed matrix. The values of EV range from 0.0 to 1.0, from no explaining to complete explanation. All of Xis explained jointly by the p

factors and by the residual, as if the residual would be an extra (p+1st) factor. Taken together, these p+1 "factors" by definition explain 100% of X. In source apportionment studies, the element number j of the (p+1st) row of EV(F) indicates how much of the variable number j remains unexplained.Whenever a value on the (p+1st) row of EV(F) exceeds 0.25, one should consider that the variable in question is practically "not explained"[70]. Profiles of EV values are useful for an intuitive indication of the significance of the factors[73], since they are a measure of the contribution of each chemical species in each source.

4.3 MULTIPLE REGRESSION TECHNIQUES

The approach to statistical analysis of the data is based on the readily justifiable assumption that PMis a mixture of materials derived from a number of independent sources. Thus, the amount of any j component present in the total sample can be expressed as the sum of contributions from each of these sources. Mathematically this is expressed, as:

$$M_j = \sum_{k=1}^{p} M_{kj} \qquad (6)$$

where M(j) is the total mass of j component present and $M_{kj}$is the mass of j component contributed by the kth source. However, each source contributes a total mass of material, F_k, of which only a fraction is j component. M_{kj} can, therefore, be represented by the product:

$$M_{kj} = a_{kj}F_k \qquad (7)$$

where a_{kj} is the concentration of j component in the total mass of material contributed by the kth source. If the compositions of material derived from all of the sources which contribute to the overall dust sample were known a priori, the present data could be fitted by standard multiple regression techniques and the contribution of each source calculated. These data are not known, but the results of multivariate statistical analysis techniques, such as PMF, fit this purpose[74].

5 Bulk deposition close to a Municipal Solid Waste incinerator: one source among many

5.1 MATERIAL AND METHODS

5.1.1 Sampling network

The studied MSWI is described in chapter 2.1.1. The sampling campaign took place from 2006 to 2010. From 2006-2008, the plant was authorized to burn a slightly lower amount waste, i.e. 127 600 t per year (maximum 10% of hospital solid waste). During the sampling period the plant worked at full capacity in 2006-2007 (3 incineration lines) and at reduced capacity in 2008-2009, due to the reconstruction process. The plant shut down its activities for six months, while for the other part of the period only one line worked, while the others were dismantled. In 2010, a new line commenced its activity.

The sampling network was designed on the basis of the dispersion map calculated by the atmospheric dispersion model Calpuff, applied to incinerator emissions. This model has been officially suggested by US-EPA as a recommended model for long-range transportation in non-steady-state conditions. Calpuff simulates the effects of temporal and spatial variations in meteoclimatic conditions on pollutant transportation, transformation, and removal. Meteoclimaticdata (wind direction, wind speed, T, P, etc.) over a 3- year period were provided by Regional Environmental Protection Agency, based on Calmet meteorological model (ARPA database, www.arpa.emr.it/sim/?osservazioni_e_dati/datiqaria). The three stacks of the considered incineration plant (point source) are 40 m high, have an inner diameter respectively of 1.1 m for the first two lines and 1.5 m for the third one. In each line the average linear emission velocity is of 15 m/s and the emission exit temperature of 433 K[22]. The modeling study was performed in a previous study which was commissioned by the plant owner. The modeling study is not therefore part of the PhD research project; its results, i.e. the dispersion map, were only used for the site choice.

The study area, together with an orographic map and an indication of sampling sites appear in Figure 5.1.

The incinerator is located in a valley; the model identifies the main fallout zone on the surrounding ridge (Figure 5.1b). Indeed, the hill ridge height varies from 60 to 70 m ASL,

which is almost the same height as the emission stack of the incinerator. According to the model, most of pollutants emitted from the stack hits against the hill ridge; furthermore, since the presence of the ridge, the dispersionof the remaining pollutants beyond the surrounding hills increases. Three sites (1, 2 and 3) are located on the hill ridge. Site 1 was located 1.8 km from the plant, in an area strongly affected by incinerator emission fallout and by the nearby A14 highway (800 m). Site 2 was placed in a rural area 1.2 km from the plant, in the main incinerator emissions fallout zone; site 3 is the same site used for the PM sampling campaigns described in chapter 2 and 3. As reported in the detailed description in chapter 2.1.1, it is not only affected by incinerator emissions, but also by pollutants coming from the coast and from road traffic. Finally, site 4 was located 4 km from the plant, in a zone of minimum fallout and used as a control site. Since it is located beyond the hill ridge it is not affected by plant emissions but it is sufficiently close to other sites to have the same background contamination.

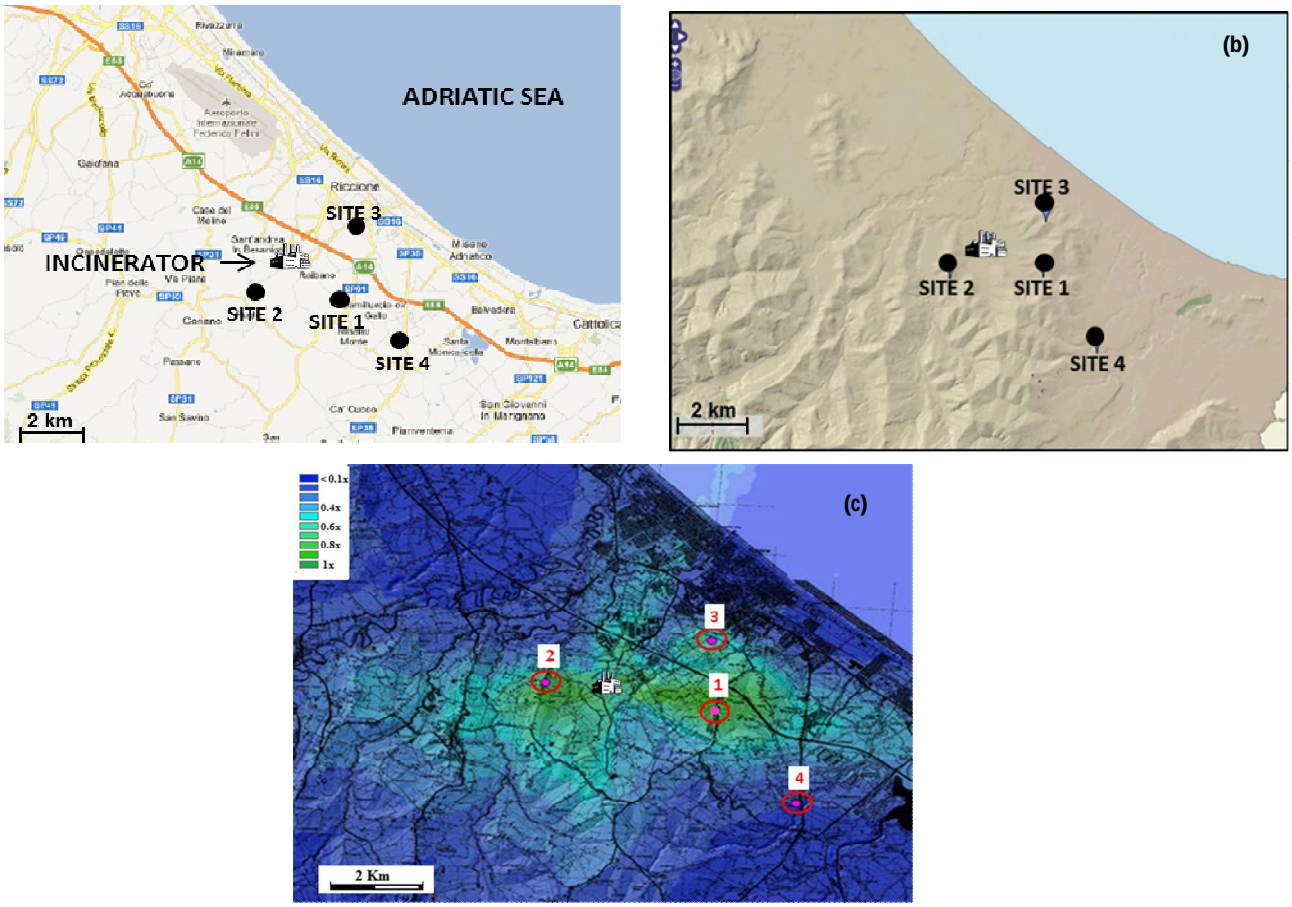

Figure 5.1: Studied area and monitoring sites on thegeneral map (a) (from Map data © 2012 Google – modified), (b) on an orographic map (from Emilia-Romagna website: http://geo.regione.emilia-romagna.it/geocatalogo/) and on the map of mean deposition fluxes of particulate from the incineration stack. The extent of deposition in the different areas is scaled according to a relative range(depending on the concentration of the studied pollutant in the emission).

5.1.2 Meteoclimatic conditions

Pollutant dispersion and deposition are affected by meteoclimatic conditions. Wind data were provided by Arpa SIM (ServizioIdroMeteorologico) Emilia Romagna.The average over the 5-year period (2006–2010) is reported in Figure 5.2. Results confirm, as previously reported in Morselliet al.[75], that wind direction (south-west -north-east) and speed are mainly dominated by the land and sea breezes. Since rainfall contributes to atmospheric pollutant removal, it influences atmospheric deposition collection by bulk samplers. The rainfall trend (mm of rain for month) from 2006 to 2010 is very variable (Figure 5.3). In 2006 rainfall was heavy in summer and light in winter, while in other years rainfall followed the typical seasonal trend; it was almost absent in the warmest months and heavier in cold months. In 2010, May and June also were particularly rainy. More details on meteoclimatic conditions are reported in Appendix I.

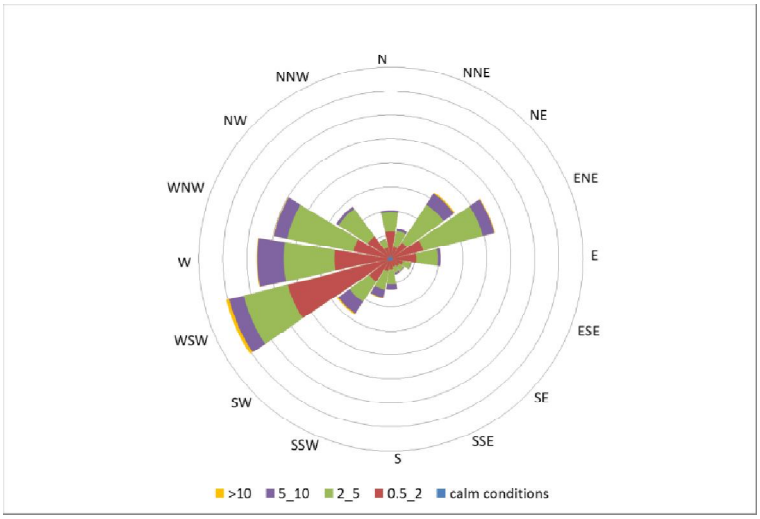

Figure 5.2:Wind rose in the study area (average of years 2006–2010).

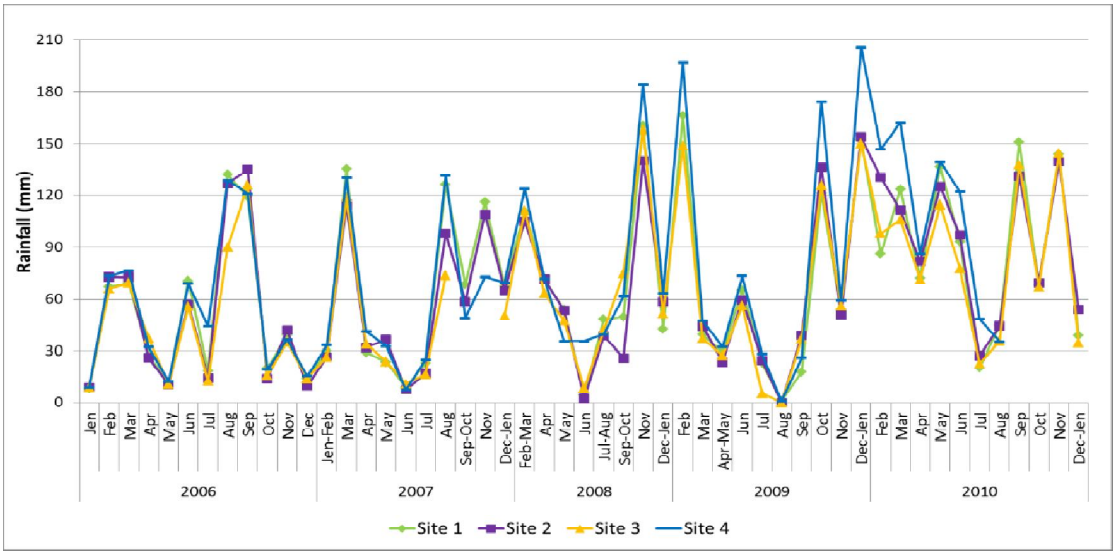

Figure 5.3:Rainfall fluxes (mm) in the sampling period

5.1.3 Sampling

Atmospheric deposition was collected monthly by Depobulk® samplers. They consist of an HDPE funnel directly connected to a collection bottle and placed in a PVC structure hanging from a pole 2 m from the ground. Bulk sampler characteristics are those recommended by Italian National Institute of Health (ISS)[76] and CEN EN 15841 method[77]. Before environmental exposure, the collecting bottles (20 l) were carefully washed using a 0.2% solution of HNO_3, then by distilled water and lastly bi-distilled water.

5.1.4 Sample preparation and analysis

After collection, samples were immediately sent to the laboratory, where they were weighed for the determination of total precipitation; then atmospheric deposition samples were filtered through cellulose nitrate filters (Millipore, 0.45 µm), in order to separate the soluble and insoluble fractions. All filters were stored at 4°C until mineralization, whereas two 250 ml representative aliquots of water solution were collected and stored in HDPE bottles at 4°C until metal and ion analysis. HNO_3 (65%, Suprapur, Merck) was added to the aliquot for metals determination, until pH<2.

For the determination of metals in the insoluble fraction, filters were mineralized in a Multiwave microwave oven. Each was placed in a Teflon bomb with 5 ml of HNO_3 and

0.5 ml HCl (30%, Suprapur, Merck). The procedure did not allow a complete digestion of silicate. However for the application of this study, i.e. having information of contaminant flux in the environment, the results are fit for purpose. Digested solution was made up to 50 ml with bi-distilled water.

Metals (Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) and soluble ions (NH_4^+, Ca^{2+}, Na^+, Mg^{2+}, K^+, Cl^-, F^-, NO_2^-, NO_3^-, SO_4^{2-}) analysis was undertaken by AAS and by Ion Exchange Chromatography, respectively; instrumental conditions as reported in chapter 3.1.2.

5.1.5 Quality assurance

Quality assurance information is reported in Table 5.1. Recovery results are based on analysis of the NIST standard reference material (SRM), 1648 urban dust (mean values for four tests). Al, Cd, Cu, Mn, Ni, Fe and Pb recoveries generally ranged from 80% to 120% , with a standard deviation always lower than 7% (for cadmium it is little higher, 10%). Zinc recovery is quite high, 144%, but RSD is good (6%). On the contrary As and Cr recoveries are low, 55% for the first and 44% for the latter. Nevertheless As and Cr fluxes are low and the study area can be considered weakly contaminated by these metals. RSD (9% for both) demonstrates that the reproducibility is good. Since the main aim of the study is the comparison among sampling sites, we decided not to discard Zn, As and Cr results.

Blank filters were digested with the same procedure as samples, to assess filter contamination. As and Cd blank values were below the graphite furnace AAS LoQ. For other metals, blank filter and sample concentrations were compared. If a sample concentration is lower than 10 times filter blank concentration,it can be considered influenced by blank filter contamination. Only few samples (Table 5.1) showed this characteristic, therefore it can be concluded that blank contamination did not significantly affect sample results. Nickel and zinc showed higher contamination; 18% of samples for the former and 12% for the latter showed a concentration lower than 10 times the blank values. Since PMF analysis allows association of an error with each value, it was decided not to discard these data as the weighting process in PMF would allow for the greater uncertainties.

Table 5.1: Instrumental LoQ, blank filter metal concentrations, number of analyzed samples affected by blank filter contamination, recovery and RSD for NIST SRM 1648 digestion procedure.

	Al	Mn	Cr	Cu	Pb	As	Ni	Cd	Fe	Zn
LoQ graphite furnaceAAS (ppb)	2.00	0.20	1.70	0.25	1.00	1.70	1.00	0.025	1.00	0.20
Blank filters concentration(ppb)	42.00	1.00	1.90	1.30	2.50	<LoQ	2.10	<LoQ	3.70	16.00
Number of analyzed samples which registered a concentration lower than 10 times filter blank concentrations	0	0	5 (3%)	1 (0.5%)	3 (1%)		39 (18%)		0	26 (12%)
Recovery values for NIST SRM 1648 (%)	82	82	51	82	118	55	100	84	94	144
RSD for NIST SRM 1648 (%)	7	4	27	2	7	9	3	10	4	6
	Na^+	**NH_4^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**SO_4^{2-}**	**NO_3^-**	**Cl^-**	**F^-**	**NO_2^-**
LoQ ion chromatograph(ppm)	0.02	0.02	0.05	0.05	0.05	0.1	0.1	0.08	0.05	0.01

5.1.6 Enrichment Factors (EF)

Atmospheric deposition is affected by the contribution of resuspended crustal material. EF determination allows a distinction between anthropogenic and natural origins of a certain element[78]. The enrichment factor calculation is based on standardization of the measured element against a reference element, assumed to be completely of crustal origin. In this work, Al was used.

$$EF(M)_{atm.dep} = \frac{(F.d.D_M / F.d.D_{Al})}{([M]_{soil} / [Al]_{soil})} \quad (8)$$

where

$F.d.D_M$ = Daily deposition flux of metal (M) (mg/m^2 d)

$F.d.D._{Al}$ = Daily deposition flux of Al (mg/m^2 d)

[M]soil = Metal concentration in soil (mg/Kg ss)

[Al]soil = Al concentration in soil (mg/Kg ss)

Soil composition was determined by chemical analysis of soils sampled in the study area in January 2011.

5.1.7 Positive Matrix Factorization (PMF)

The unit of measurement has been chosen in order to have data values not extremely small or extremely large. For this reason, deposition fluxes of F^-, NO_2^-, As, Cd, Cr, Cu, Mn, Ni, Pb, and Zn were expressed in µg/(md), while deposition fluxes of Fe, Al, SO_4^{2-}, NO_3^-, Cl^-, Ca^{2+}, Na^+, NH_4^+, Mg^{2+} and K^+ in mg/(m^2 d).Standard deviations (s_{ij}) were calculated with EM=-12 option (Equation 3, chapter 4.2). In this study C1 was specified individually for each measurement (standard deviations matrix). For each value x_{ij}, the standard deviation was computed as 1/3 of the method detection limit of the sample plus 10% x_{ij}, which was considered as the measure uncertainty[10]. For the missing values, arbitrary high values of standard deviations were used. C2 was =0, as usually used[70], while for C3, different values between 0.04 and 0.25 were tested[69,79].

The Robust mode, together with the value of four times the S.D. of the species to define outliers, was used to minimize the distortion of dataset by the outliers[80]. Since there are some missing data and a lot of data below the detection limit, the optional parameter "BDLneg r1 r2" was used. As suggested by Paatero[70], r2=10 was used.

In PMF, the choice of the number of factors is a compromise. Using too few factors will combine sources of a different nature together. Using too many factors will make a real factor further dissociate into two or more nonexistent sources[73].

The appropriate number of factors extracted and the value of C3 were then determined based on satisfying most of the following criteria (the first four criteria were based on Lee et al.[73] and Chan et al.[80]:

- Value of Q close to n x m – p x m – p x n (i.e. the degree of freedom of the analysis).
- R90 (the 90 percentile of the scaled residuals, r_{ij}) is within ±2. That is, most of the residuals are within 2.

- A sharp drop in IM (the maximum of the mean values of r_{ij} of each species) and/or IS (the maximum of the S.D. of r_{ij} of each species). Generally speaking the more the factors, the better the fit. IM and IS serve as indicators to identify the species having the least fit and the most imprecise fit, respectively. When the number of factors increases to a critical value, IM and IS will experience a drastic drop.

- A significant increase in the largest rotmat element. A small number of factors should be chosen, since by increasing the number of factors, the largest rotmat element sharply increases.

- Comparison of the mass profile of the marine aerosol factor with sea water composition[81]

- Comparison of the resuspended soil dust mass profiles factor with the composition of the soil in the study area, by comparison of the Ca/Al ratio and the Fe/Al ratio in soil and in the PMF profile.

Three to 11 factor solutions were tested, but only six factors and C3=0.12 were found to obey all the required constraints and resulted in a physically meaningful solution (see Figure 5.4 for IM, IS and ROT values for C3=0.12). The optimal Q-value obtained with this model was 3192, which compares reasonably well with the theoretical value of 2638 for the six factor model. The observed difference between theoretical and calculated Q-value (factor of 1.2) is reasonable given the empirical nature of the equations used for estimating the input error values and the presence of missing points[79]. R90 is within ±2. Specifically, 94% of the residuals are within ±2. Six factors explained >75% of the variations in most species; however >30% of the variations in As, Fe and Pb were not explained by these factors. These species have large number of samples which have concentrations below the detection limit; this could be the reason for such a high variation explained by residuals[80].

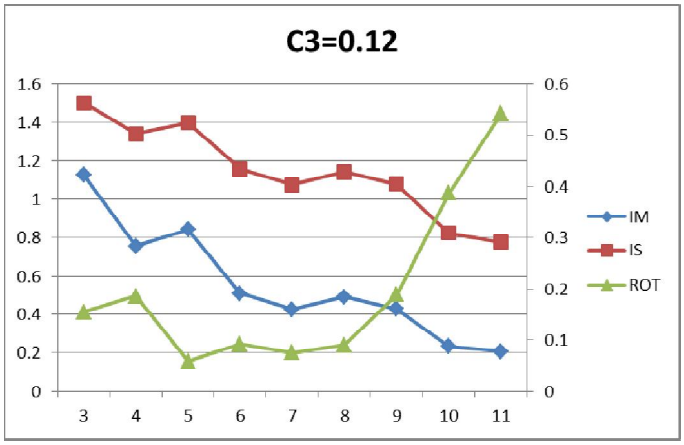

Figure 5.4: Determination of the number of factors, using C1=0.12

5.2 RESULTS AND DISCUSSION

5.2.1 Inorganic ions

Fluxes of ions were calculated according to the formula:

$$F = \frac{[A]*V}{fs*t}$$

where:

F = flux (mg/(m^2 d));

[A] = component concentration (mg/l);

V= volume collected (l)

fs = funnel surface area (m^2);

t= deploying time (days)

Mean daily deposition fluxes of inorganic ions registered at the different sites are reported in Appendix II. Fluxes of most analytes monitored during the same period, are quite similar from one site to another. Generally, no large differences can be seen among the values found at the most affected sites (according to the dispersion model, i.e. sites 1, 2 and 3), and the reference site (site 4). On the contrary, temporal variability is quite high. Nitrate fluxes decreased from 2006 to 2010, especially at sites 1, 2 and 3, and in the last

years deposition fluxes were similar to site 4. In comparison with another study undertaken in the same region[82], deposition fluxes show a high load of chloride and sodium due to the influence of the coastal area, while nitrates, sulfates and ammonium fluxes are lower.

In order to assess the differences between the most affected sites and the reference one, the per cent difference of ionic load with respect to the control site for each of the sites 1 to 3 has been evaluated for each month. In Figure 5.5 median, lower and upper quartile are reported for each component.

Potassium, ammonium, nitrate and nitrite usually show a lower flux at site 4. Specifically, more than 60% of data show a higher flux at the most affected sites. For ammonium at site 2 and nitrate at site 3, more samples show a lower flux at site 4, 82% for the former and 75% for the latter.

In order to better evaluate inter-site differences for each chemical species, a significance test was also used. First of all the frequency distribution of the concentrations was examined, represented by the mean daily deposition fluxes for each month. All the chemical species proved to be log-normally distributed (goodness of fit was tested with the Kolmogorov-Smirnov method) except for nitrite, nitrate and ammonium. For these species, the non-parametric Mann-Whitney test was used, while for the others a t-test, using the logarithm of deposition fluxes, was used. Usually the null hypothesis (i.e. there is no difference between the two mean values) is rejectedif the probability of such a difference occurring by chance is less than 1 in 20 (i.e. 0.05 or 5%). In such a case the difference is said to be significant at the p=0.05 (or 5%) level[83].Deposition fluxes of nitrite and ammonium at site 4 were confirmed to be significantly lower (p-level 0.05) than at other sites.

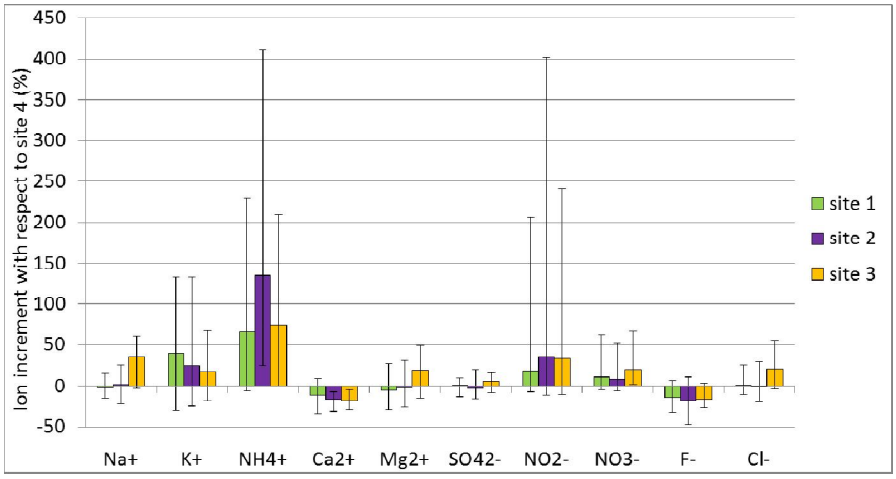

Figure 5.5: Ionic deposition median difference at sites 1, 2 and 3 with respect to site 4 for each ionic component. The bars represent the upper and lower quartile.

A preliminary study on the origin of the ions in the area used Pearson correlation coefficients between deposition fluxes of ions for each site (Table 5.2a-d). A significant correlation may be reflective of a common source of contaminants. At all sites, ions due to the marine spray contribution (Cl^-, Na^+, Mg^{2+} and SO_4^{2-}) correlated significantly ($p=0.001$), indicating a strong contribution of sea spray. This is the only source that can be identified with this technique. There are other significant correlations, but they did not occur at all 4 sites and are not typical of any known emission source.

Table 5.2: Intra-site Pearson correlation coefficients among the soluble ions at site 1(a), 2 (b), 3 (c) and 4 (d). Significant correlations (p=0.001) are reported in bold

Site 1	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	NO_3^-	Cl^-	F^-	NO_2^-
Na^+	1.00									
NH_4^+	-0.05	1.00								(a)
K^+	0.12	0.41	1.00							
Ca^{2+}	0.43	0.08	0.28	1.00						
Mg^{2+}	**0.65**	-0.04	0.10	0.32	1.00					
SO_4^{2-}	**0.74**	0.16	0.03	0.38	**0.67**	1.00				
NO_3^-	0.19	0.05	0.15	0.18	0.17	0.11	1.00			
Cl^-	**0.75**	-0.01	0.27	0.37	**0.92**	**0.80**	0.24	1.00		
F^-	0.21	0.23	**0.47**	0.45	**0.59**	**0.55**	0.32	**0.70**	1.00	
NO_2^-	-0.05	-0.02	-0.01	-0.07	-0.10	-0.09	-0.07	-0.06	-0.09	1.00

Site 2	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	NO_3^-	Cl^-	F^-	NO_2^-
Na^+	1.00									
NH_4^+	0.01	1.00								(b)
K^+	0.27	0.16	1.00							
Ca^{2+}	0.30	-0.07	0.17	1.00						
Mg^{2+}	**0.69**	0.00	0.18	0.44	1.00					
SO_4^{2-}	**0.76**	0.21	0.28	0.41	**0.64**	1.00				
NO_3^-	0.24	0.07	0.16	0.40	0.44	0.41	1.00			
Cl^-	**0.78**	0.03	0.20	0.39	**0.91**	**0.84**	0.36	1.00		
F^-	-0.02	0.13	0.13	0.09	0.10	0.22	0.27	0.25	1.00	
NO_2^-	-0.12	0.12	0.01	-0.12	-0.12	-0.08	-0.29	-0.09	-0.06	1.00

Site 3	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	NO_3^-	Cl^-	F^-	NO_2^-
Na^+	1.00									
NH_4^+	0.07	1.00								(c)
K^+	0.29	-0.06	1.00							
Ca^{2+}	0.20	-0.19	0.44	1.00						
Mg^{2+}	**0.83**	0.06	0.33	0.41	1.00					
SO_4^{2-}	**0.75**	-0.02	**0.49**	**0.66**	**0.78**	1.00				
NO_3^-	0.27	0.39	0.17	**0.48**	0.42	**0.53**	1.00			
Cl^-	**0.72**	0.27	0.21	0.30	**0.92**	**0.85**	**0.62**	1.00		
F^-	-0.07	0.27	0.08	0.07	-0.03	0.13	0.32	0.17	1.00	
NO_2^-	0.04	-0.06	-0.02	0.05	0.03	0.05	-0.04	-0.03	-0.09	1.00

Site 4	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	NO_3^-	Cl^-	F^-	NO_2^-
Na^+	1.00									
NH_4^+	0.12	1.00								(d)
K^+	0.21	0.22	1.00							
Ca^{2+}	0.23	-0.31	-0.01	1.00						
Mg^{2+}	**0.72**	0.03	0.33	0.41	1.00					
SO_4^{2-}	**0.73**	0.32	0.41	0.22	**0.68**	1.00				
NO_3^-	0.36	0.31	0.34	0.18	**0.56**	**0.50**	1.00			
Cl^-	**0.76**	0.16	0.42	0.27	**0.94**	**0.82**	0.44	1.00		
F^-	-0.05	-0.06	-0.02	0.34	-0.06	0.09	0.06	0.02	1.00	
NO_2^-	0.13	-0.06	-0.05	0.08	0.05	0.03	0.06	0.06	-0.04	1.00

5.2.2 Heavy metals

Even if metal solubility can provide insights into the origin of the metal itself[84], it is influenced by several other factors, such as pH, anion-cation balance, redox potential, temperature, complexing agents and so on. For this reason, even though metals were determined separately in the soluble and the insoluble fractions, results will be discussed by considering the sum of the two fractions.

Mean daily deposition fluxes of heavy metals registered each month are reported in Appendix 3. The per cent differences of metal load with respect to the control site for each of the sites 1 to 3 for each month were calculated. Median and lower and upper quartiles for each component are reported in Figure 5.6.Considering the total sampling period (2006-2010), a high variability can be observed and it was concluded that there are no important spatial differences in the area.The study area is characterized by a low metal load, similar to other suburban areas[84,85].

Since all the species are log-normal distributed, the t-test significance test was applied. Deposition flux of copper at site 4 is significantly higher than at site 1 and 2, while the p-value for site 3 is 0.06. Copper can be a marker of several processes, such as vehicular traffic (brake wear emissions)[86,87]and also municipal solid waste incineration[88]. Since copper is the only vehicular traffic marker higher at site 4 and the location of the site itself, the greatest contribution to copper may be due to copper fungicide used on the nearby agriculture land[89,90].

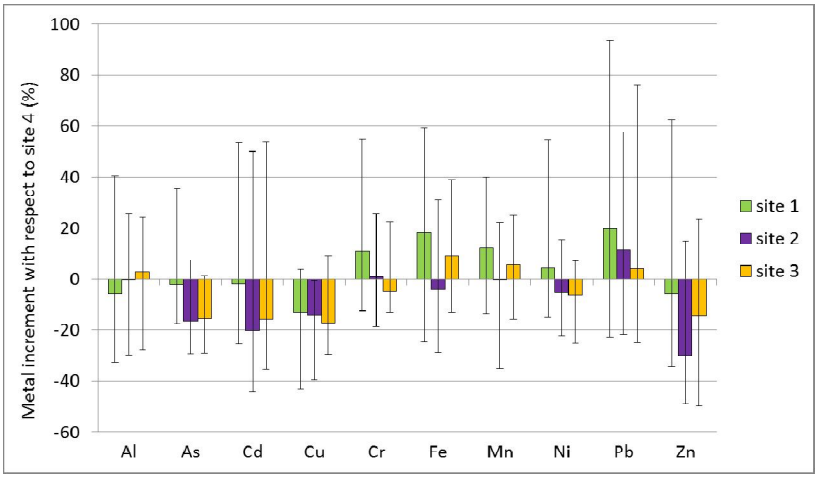

Figure 5.6: Median deposition difference at sites 1, 2 and 3 with respect to site 4 for trace metals. The bars represent the upper and lower quartile.

Table 5.3a-d reports Pearson correlation coefficients among deposition fluxes of metals for each site. At all sites, major constituents of soil (Fe, Al and Mn) correlate significantly (p=0.001), indicating a contribution of resuspended soil dust. At some sites, Cr also correlates with these metals, indicating that the presence of Cr in atmospheric deposition is mainly due to the contribution of the soil. Other significant correlations are Cu-Ni and Cu-Pb at site 2, Zn-Ni at site 3 and Cu-Ni and Cu-Zn at site 4. Cu, Zn and Pb could be markers of the incinerator[88], but the Cu-Zn correlation is significant also at site 4 and these elements correlate significantly also with Ni, which is a marker of oil combustion, and may be related to vehicular traffic emissions[61,62]. These correlations appear to indicate the contribution of vehicular traffic, since Cu, Pb and Zn are markers also of this source[61,62,86].

Table 5.3: Intra-site Pearson correlation coefficients among metals and arsenic at site 1(a), 2 (b), 3 (c) and 4 (d). Significant correlations (p=0.001) are reported in bold

Site 1	Al	As	Cd	Cu	Cr	Fe	Mn	Ni	Pb	Zn
Al	1.00									
As	0.17	1.00								(a)
Cd	-0.15	-0.15	1.00							
Cu	-0.14	0.05	0.10	1.00						
Cr	**0.52**	0.44	0.12	-0.08	1.00					
Fe	**0.74**	0.17	0.00	-0.05	0.44	1.00				
Mn	**0.75**	0.23	-0.22	-0.01	**0.66**	**0.74**	1.00			
Ni	0.40	0.27	0.29	0.31	**0.64**	**0.50**	**0.52**	1.00		
Pb	-0.07	-0.05	0.04	0.29	-0.13	-0.05	-0.08	0.03	1.00	
Zn	0.03	0.14	0.30	0.26	0.21	0.20	-0.08	0.33	0.39	1.00

Site 2	Al	As	Cd	Cu	Cr	Fe	Mn	Ni	Pb	Zn
Al	1.00									
As	-0.08	1.00								(b)
Cd	-0.10	-0.14	1.00							
Cu	-0.13	-0.09	-0.15	1.00						
Cr	0.27	0.45	-0.23	-0.08	1.00					
Fe	**0.74**	-0.12	-0.03	-0.04	0.25	1.00				
Mn	**0.46**	-0.10	-0.19	0.17	0.38	**0.49**	1.00			
Ni	0.34	0.09	-0.13	**0.48**	0.34	0.20	0.27	1.00		
Pb	-0.09	0.04	0.05	**0.51**	-0.06	-0.23	-0.01	0.42	1.00	
Zn	-0.06	**0.55**	0.17	-0.03	**0.51**	-0.04	-0.03	0.12	-0.09	1.00

Site 3	Al	As	Cd	Cu	Cr	Fe	Mn	Ni	Pb	Zn
Al	1.00									
As	0.06	1.00								
Cd	-0.07	-0.05	1.00							
Cu	0.06	0.06	0.19	1.00						
Cr	0.40	-0.02	0.28	0.17	1.00					
Fe	**0.76**	0.08	-0.03	0.37	0.38	1.00				
Mn	**0.72**	0.29	-0.16	0.14	0.36	**0.57**	1.00			
Ni	-0.02	-0.02	0.04	0.17	0.22	-0.01	-0.04	1.00		
Pb	-0.05	0.00	-0.07	0.15	0.14	-0.01	-0.09	0.15	1.00	
Zn	0.04	0.08	0.13	0.44	0.37	0.06	0.01	**0.65**	0.14	1.00

(c)

Site 4	Al	As	Cd	Cu	Cr	Fe	Mn	Ni	Pb	Zn
Al	1.00									
As	0.09	1.00								
Cd	0.01	0.01	1.00							
Cu	0.16	0.19	0.49	1.00						
Cr	0.44	0.04	0.09	0.13	1.00					
Fe	**0.59**	0.37	0.36	0.34	0.36	1.00				
Mn	**0.57**	0.30	-0.09	0.05	**0.65**	**0.63**	1.00			
Ni	0.47	0.12	0.41	**0.62**	**0.52**	0.44	0.37	1.00		
Pb	0.00	-0.05	0.07	0.42	0.04	-0.03	-0.12	0.20	1.00	
Zn	0.19	0.23	0.40	**0.64**	0.04	0.46	0.13	0.42	0.26	1.00

(d)

The enrichment factor (EF) may help to identify a resuspended soil dust contribution and thus an external contribution which is generally, but not always anthropogenic (Table 5.4). Usually anthropogenic contamination is considered significant if EF>100, modest if 10<EF<100 while the origin is mainly natural if EF<10[78]. EF data (Table 5.4) confirm that Cr and Mn are mainly due to resuspended soil dust, as indicated by the Pearson correlation coefficients. According to the EF, Ni also is mainly due to the soil contribution. Deposition fluxes of Cd are usually below the method detection limits, as for As, so it is difficult to interpret information from its EF. However, in 2010, the deposition flux of Cd was above the method detection limit and the EF indicates that it is mainly due to resuspended soil dust. Cu, Pb and Zn are instead due to anthropogenic sources. For Cu and Pb the EF decreased from 2006 to 2010 and they are lower than 10 in the last year, indicating a mainly natural source. These metals could be considered as markers both of vehicular traffic and incineration plants, but since similar values of EF were registered at site 4 and at other sites, they seem most probably due to vehicle emissions.

Table 5.4: Enrichment factors of metals in bulk deposition.

*	site1					site2					site3					site4				
	200	200	200	200	201	200	200	200	200	201	200	200	200	200	201	200	200	200	200	201
Cr	**1.3**		**0.9**	**1.9**	**1.1**	**1.8**		**1.2**	**2.0**	**1.2**	**1.9**		**1.0**	**2.1**	**1.3**	**1.2**		**1.0**	**2.4**	**0.6**
Cu	<41	19	9	6	6	<42	14	15	9	6	<40	27	12	13	6	<36	19	17	16	5
M	1.3	0.8	1.0	1.3	0.7	1.5	0.6	1.4	1.4	0.8	**1.5**	1.2	1.2	1.4	0.8	1.1	**0.5**	1.2	1.4	0.6
Ni	<5.	<2.	**1.1**	<2.	**0.8**	<4.2	**1.2**	**1.3**	**1.4**	**0.9**	<5.3	**1.8**	**1.3**	**1.5**	**0.9**	<3.	**1.5**	**1.5**	<2.	<0.
Pb	47	27	**7.1**	**6.9**	**7.3**	<78	11	**10.4**	**8.9**	**8.9**	**57**	15	**14.2**	**10.5**	**6.8**	**69**	23	**11.1**	<13	**3.7**
Zn	52	67	17	16	18	31	32	20	19	29	40	70	22	21	19	50	38	38	26	14
As	<68	<15	<55	<65	<37	<82	<10	<77	<64	<41	<11	<14	<76	<61	<30	<62	<10	<93	<75	<20
Cd	<62	<93	<16	<4	4	<10	<81	<19	<4	4	<15	<85	<19	<5	11	<12	<42	<25	<8	4

*Often metal concentration in atmospheric deposition resulted below the detection limit (BDL). When in both the dataset (soluble and insoluble fraction) 50% of the annual values at least were BDL, the annual flux was calculated by using the detection limit for a BDL value and the enrichment factor was reported as "lower than". When only in one dataset (soluble or insoluble) 50% of the annual values at least were BDL, the fraction which makes the highest contribution to the total flux was considered. If it were the fraction with 50% of the annual values at least BDL, the annual flux was calculated by using the detection limit, for a BDL value, and the enrichment factor was reported as "lower than". If it were the other, annual flux was calculated by using ½ DL for BDL value, as suggested by Italian National Institute of Health (ISS)[91]. The enrichment factor is reported in bold and it is just an estimate of the real value

5.2.3 Positive Matrix Factorization

The overall mass concentration profiles of the six factors affecting the four sites are shown in Figure 5.8. The first factor consists of mainly potassium, calcium and iron, but also sodium, magnesium and sulfates give an appreciable contribution. This factor is characterized by elements typical of Saharan dust, in particular of the western part of the region, which is richer in calcium rather than aluminum[92,93]. Temporal trends of the factors (Figure 5.9) show that in March-April 2007 the contribution of this factor at the sites was about 10 times higher than the mean value. The study area is often characterized by Saharan dust events and probably they were particularly strong in this month. In order to confirm this event, back trajectories were studied. Site 3 was considered as the arrival point, but other sites will be affected by the same back trajectories. A transport time of 48 hours was considered suitable to assess long-range contributions. In Figure 5.7 an example which considers the period 23-26 March 2007 is reported. Meteorological parameters of the database GDAS1 and an arrival level height of 2 m AGL were chosen as input data. Back trajectories were computed by the HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model for calculating air parcel trajectories for complex dispersion and deposition simulations. Back trajectories confirmed a Saharan dust event.

The second factor is more difficult to interpret, since it is characterized by Zn, Cu, Pb, Fe and Cd, which can be markers both of vehicular traffic and incinerators[73,78,80,94,95,96]. For this reason it was called "Metals". Cl^- is not represented by this factor and since it is also a marker of incineration[97], this suggests that vehicular traffic is better represented by this factor. However Cl^- has been reported also in a vehicular emissions factor[73,95]. Further insights can be gained by considering the factor contribution at each site (Figure 5.9). In 2009-2010, the temporal contribution of this factor at each site decreased. In 2008 the incinerator was reconstructed, possibly giving an explanation for this behavior. However, in 2008 the plant was closed entirely for six months, but the contribution of the factor is higher than in 2009-2010. Additionally, the contribution at site 4 is not lower than at the other sites. For these reasons, this factor is very unlikely to be associated with the incinerator and is more probably due to vehicular traffic.

The third factor is characterized by the chemical species present in sea water, i.e. Na^+, Ca^{2+}, Mg^{2+}, SO_4^{2-} and Cl^-, so this factor represents the marine aerosol contribution. One of the criteria chosen to evaluate the solution obtained with PMF analysis is comparison of this factor with sea water composition[81]**.** The results are reported in Table 5.5. They are quite similar. The major difference between the two profiles is due to the lower % of chloride in the PMF profile, which is balanced out with a higher contribution of nitrate and sulfate. The deficit of chlorine, referred to as "chlorine depletion", is caused by reactions of acids (i.e. H_2SO_4 and HNO_3) not completely neutralized by ammonia, with sodium chloride to expel HCl. As a result, $NaNO_3$ or $Ca(NO_3)_2$ are produced in the particle[73,98,99]. The sum of these three anions is very similar in sea water and in the PMF profile.

Temporal trends of the factors indicate that the marine spray contribution is particularly high during some months (Figure 5.9). In order to better understand these events, mean hourly wind direction and speed were assessed. It was possible to conclude that in general marine spray events occur when, at least for few hours (e. g. 5 hours can be sufficient) wind direction is from over the sea with a wind speed equal or higher than 8 m/s.

The fourth factor is mainly characterized by nitrates, but also by chlorides and sulfates. It could represent secondary nitrates due to the conversion of NO_x, emitted both by vehicular traffic and by other combustion processes. The absence of potassium, a marker

of biomass combustion processes is suggestive of a contribution from other sources of combustion.

The fifth factor is clearly resuspended soil dust, since it is characterized by Ca, Al and Fe but also by other metals that can be found in soil. Another criterion chosen to evaluate the solution obtained with PMF analysis is the comparison of this factor with soil composition**.** The mass profile was compared with the composition of the soil in the study area, which was sampled in January 2011. The results are quite similar. The ratio Ca/Fe in the factor is 2.84, which is similar to what is found in soil (2.99), while the Ca/Al ratio is 2.60, while in soil it is 2.03. Finally the ratio between all other analyzed metals and Ca is 0.018 in the PMF factor and 0.013 in soil.

The last factor consists mainly of ammonium and sulfate. Secondary ammonium sulfate aerosol is formed from oxidation of sulfur dioxide in the atmosphere. The ammonium found in this source accounts for more than 85% of the total ammonium concentration. The molar ratio NH_4^+/SO_4^{2-} shows that ammonium is in strong excess which is because ammonium is also associated with other species (e.g. nitrate).

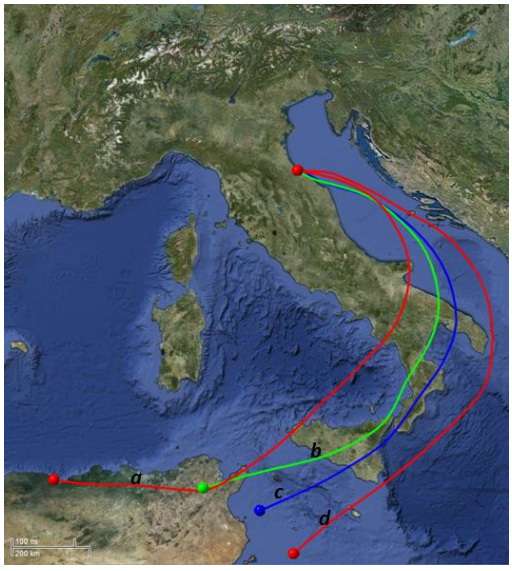

Figure 5.7: Back trajectories at site 3 for the period 23th-26th March 2007. Back trajectories time: 48 hours. a: 6.00 PM 25/03 – 6.00 PM 23/03/2007. b: 0.00 AM 26/03 – 0.00 AM 24/03/2007. c: 6.00 AM 26/03 – 6.00 AM 24/03/2007. d: 12.00 AM 26/03 – 12.00 AM 24/03/2007.

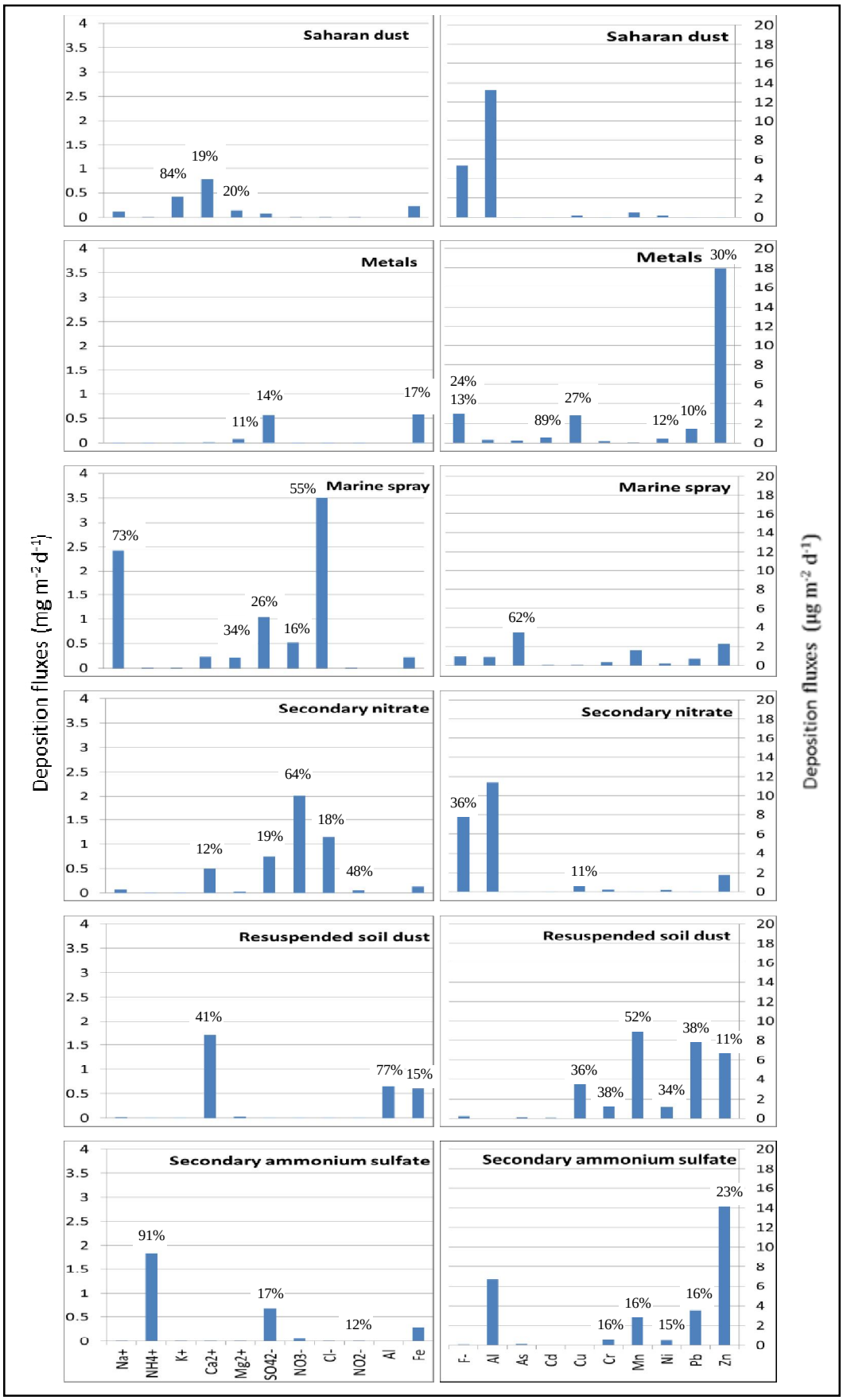

*Figure 5.8: Sources profiles in mass concentration. For each factor, the left box reports soluble ions, Fe and Al (the latter only for resuspended soil dust) profiles (mg m^{-2} d^{-1}). In the right box, Zn, Pb, Ni, Mn, Cr, Cu, Cd, As and Al (for the other five factors) profiles are reported (µg/(m^2*d^1). The percentage contribution of the factor to each chemical component is also reported*

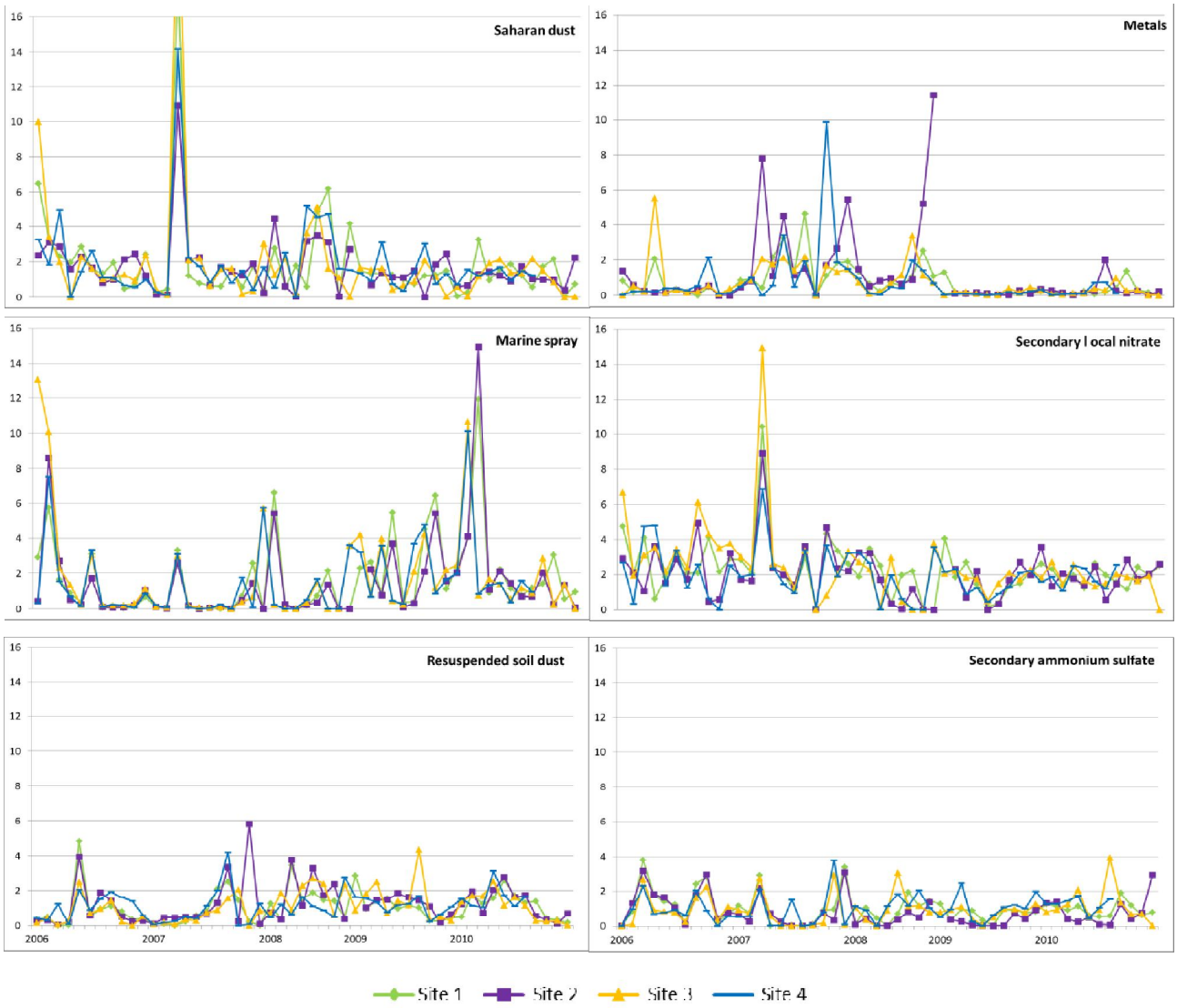

Figure 5.9: Temporal variation of source contributions at the four sites.

Table 5.5: Comparison between sea water composition and marine spray profile obtained with PMF

Ions	Composition of sea water. Mass percentage (%)	Marine spray profile by PMF. Mass percentage (%)
Na^+	30.37	29.70
SO_4^{2-}	7.81	12.64
Cl^-	54.96	42.82
K^+	1.1	0.00
Ca^{2+}	1.2	2.91
Mg^{2+}	3.9	2.72
NO_3^-		6.30
Other	0.7	2.90

Among the components analyzed, heavy metals are those which create the greatest concern, due to their toxicity and their persistence in the environment. For this reason the median contribution of each metal (Fe, As, Cd, Ni, Cr, Mn, Cu, Pb and Zn) to toxicity for each source at each site has been evaluated. The concentration of metals in each source (F matrix) has been divided by the acceptable daily intake indicated by WHO[100,101,102]. In this way, evaluation of the total load of metals giving a higher weight to the most toxic metals has been generated. The results appear in Figure 5.10. The highest contribution of metals is due to resuspended soil dust. This is especially due to lead, which together with cadmium, are the most toxic metals. The resuspended soil dust factor makes the highest contribution even when considering the sum of metals not weighted by their toxicity. Thus, not only do three of the six identified sources represent natural matrices, one of them is the main source of metals in atmospheric deposition. After resuspended soil dust, the secondary ammonium sulfate factor is the most important source of metals, and this is also due to the high concentration of lead associated with this factor.

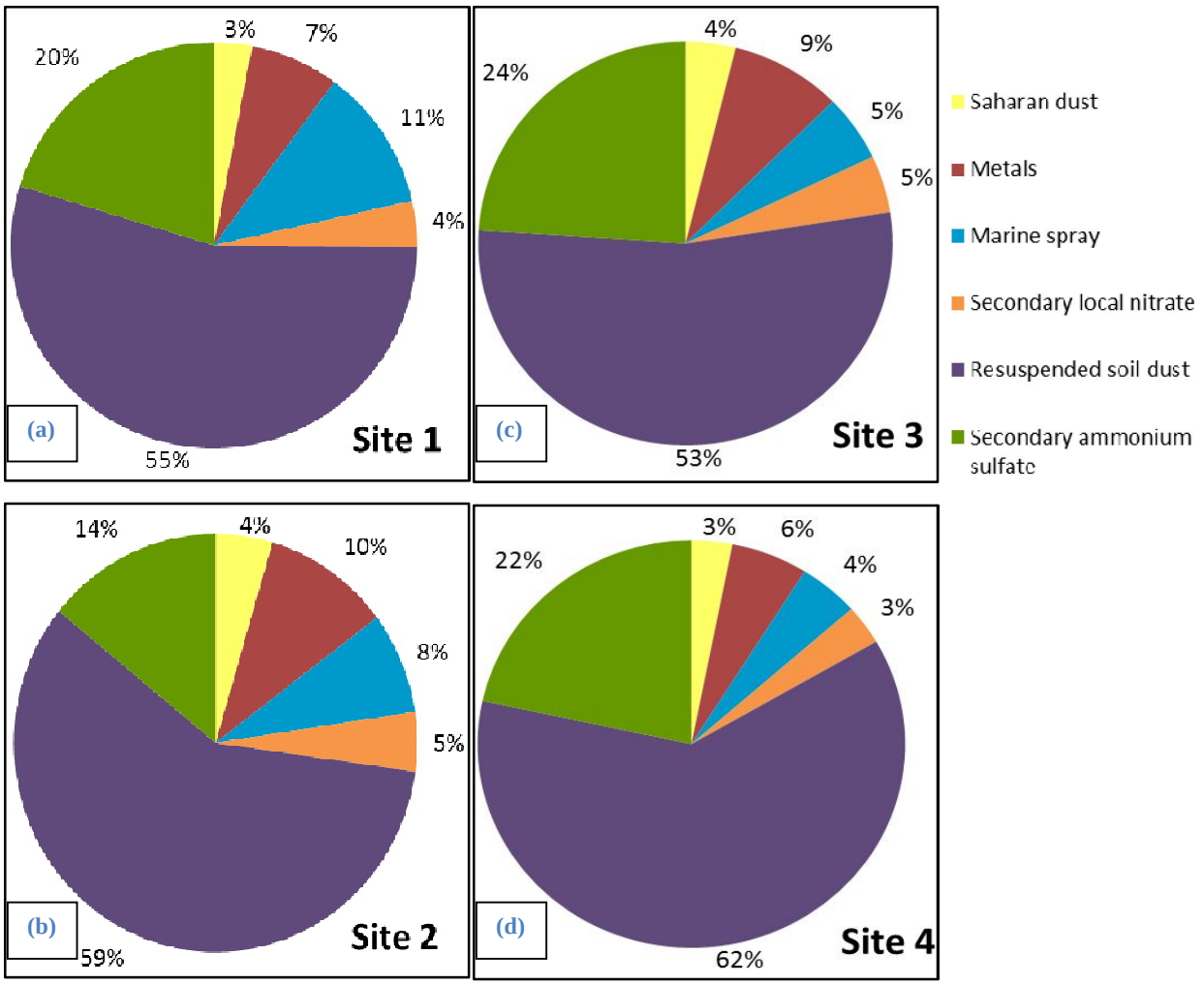

Figure 5.10:Percentage contribution of each factor to toxicity based upon the metal content weighted by relative toxicity. (a) site 1; (b) site 2; (c) site 3 and (d) site 4.

5.3 CONCLUSION

The deposition fluxes recorded in the study area show a low concentration of heavy metals and soluble ions in atmospheric deposition when compared to other studies. Only ammonium and nitrite fluxes are significantly lower at the reference site, while all other components do not show significant differences between the sites.

The whole area seems to be overall affected by a rather homogeneous contamination, suggesting that multiple sources, rather than a single hot spot emission source like the incinerator, are influencing the whole area. PMF analysis indicates that six main sources affect the area, three ascribed to natural matrices (sea spray, resuspended soil dust and Saharan dust) and three ascribed to anthropogenic sources (secondary nitrates, secondary

sulfates and another one more ambiguous, that probably represents the influence of vehicular traffic emissions). The greatest contribution of heavy metals, which are the most toxic and persistent of the analyzed components, to atmospheric deposition is due to resuspended soil dust, especially when weighted according to their toxicity.

In conclusion, the incinerator's relative contribution to the total inorganic pollutant load seems to be negligible compared to other sources affecting the area.

Atmospheric bulk deposition is useful to analyze temporal and spatial trend since the obtained results refer to monthly average data. Nevertheless, by increasing temporal resolution, probably it is possible to further investigate local source relative contribution. In order to go deeper in the analysis of the sources affecting the area, a PM sampling campaign was undertaken and samplers coupled with a wind select sensor were used.

6 Application of PMF analysis to data of daily PM collected with a wind select sampler

6.1 EXPERIMENTAL METHODS

6.1.1 Sampling

The sampling site is the same described in chapter 2.1.1. Two medium volume samplers (Skypost PM, TCR TECORA), equipped with a $PM_{2.5}$ sampling head were used. Each sampler operated at the flow rate of 38.33 l/min. In addition to these, a third sampler, (ECHO HiVol, TCR TECORA) equipped with a $PM_{2.5}$ sampling head and operating at the flow rate of 200 l/min, has been used. The samplers were coupled with a wind direction and speed sensor, which allows the turning on and off of the instrument depending on wind direction and speed. The sampling campaign was design for an alternate sampling of the air masses downwind or upwind the incinerator (Figure 6.1). The samplers switched on or when they were downwind of the incinerator ±60° (120 degree window) (Figure 6.1a), or when they were downwind of the coast ±90° (180 degree window) (Figure 6.1b). In the first condition, they collected $PM_{2.5}$ coming from the inland and influenced also by the motorway, while in the other, the samplers collected $PM_{2.5}$ coming from the coast and samples were thus influenced by the urban area. The medium volume samplers collected simultaneously $PM_{2.5}$ in the air masses coming from the same direction. At the same time, the high volume sampler collected $PM_{2.5}$ in calm condition, i.e. when wind speed was lower than 0.5 m/s.

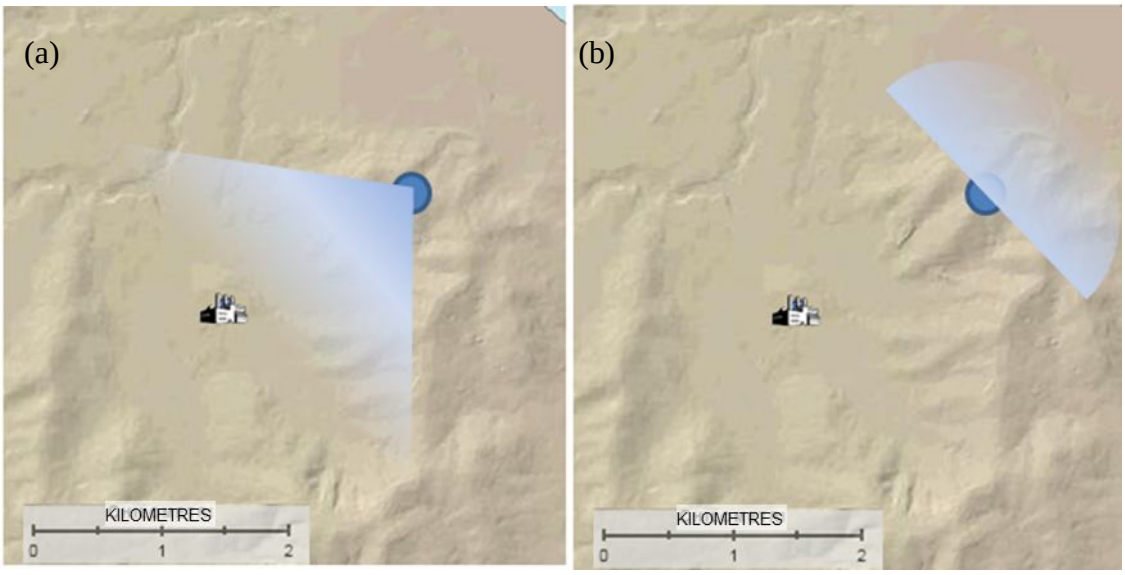

Figure 6.1: The alternate sampling conditions for medium volume samplers: (a) sampling window when the samplers collected the air masses downwind of the incinerator and(b) sampling window when the samplers collected the air masses upwind of the incinerator

The sampling campaign started on the 29th of November 2011 and finished on the 28th of April, 2012. Overall, 60 samples were collected: 31 for calm conditions, 15 influenced by air masses coming from the inland and 14 influenced by air masses coming from the coast. The input time for each sampling was 48 hours. In fact during this time interval, the samplers collected $PM_{2.5}$ only in the above mentioned wind conditions. This sampling approach is thus strongly influenced by wind conditions and during some days it was not possible to collect a sufficient amount of PM for the required analysis. Therefore the filter was left in the sampler and PM was collected for extra-hours. More details on the sampling campaign are reported in Table 6.1

Table 6.1: Sampling dates, wind influence and sampling time

Date	Wind direction	Programmed sampling time (hours)	Effective sampling time (hours)
29/11-2/12/11	calm	48:00:00	25:00:01
	inland	83:00:00	25:49:09
3-4/12/11	inland	48:00:00	32:53:02
3-7/12/11	calm	96:00:00	27:40:56
5-7/12/11	inland	48:00:00	34:04:31
10-11/12/11	calm	48:00:00	32:45:48
	coast	72:00:00	27:32:18
17-18/12/11	coast	48:00:00	17:33:57
	calm	48:00:00	8:34:58
19-21/12/11	coast	60:00:00	23:44:39
	calm	60:00:00	15.25:51
31/12/11-1/1/12	calm	60:00:00	30:18:43
31/12/11-4/1/12	coast	84:00:00	22:43:58
3-5/1/12	calm	48:00:00	13:27:48
10-11/1/12	inland	48:00:00	36:21:29
	calm	48:00:00	27:26:30
14-15/1/12	calm	48:00:00	26:40:48
	inland	48:00:00	34:34:43
17-19/1/12	calm	60:00:00	48:53:17
	coast	60:00:00	36:05:42
21-22/1/12	coast	48:00:00	16:20:38
25-26/1/12	calm	48:00:00	15:18:56
	inland	48:00:00	33:17:52
28-19/1/12	calm	48:00:00	30:35:51
	inland	48:00:00	18:41:30
1-2/2/12	coast	48:00:00	18:24:50
11-12/2/12	coast	48:00:00	19:27:13
18-19/2/12	calm	48:00:00	28:30:24
25-26/2/12	calm	48:00:00	21:14:06
29/2-1/3/12	calm	48:00:00	25:08:26

Date	Wind direction	Programmed sampling time (hours)	Effective sampling time (hours)
3-4/3/12	calm	48:00:00	27:23:16
	inland	48:00:00	24:28:02
7-8/3/12	inland	48:00:00	27:16:47
	calm	48:00:00	23:13:29
10-13/3/12	calm	48:00:00	7:47:57
	coast	72:00:00	31:32:16
14-15/3/12	calm	48:00:00	30:00:14
18-19/3/12	calm	48:00:00	10:26:38
	coast	48:00:00	12:08:16
21-23/3/12	calm	48:00:00	32:38:42
	inland	48:00:00	22:00:23
24-25/3/12	calm	48:00:00	16:15:11
	inland	48:00:00	26:25:50
26-28/3/12	calm	48:00:00	21:30:06
	coast	48:00:00	22:12:58
31/3-1/4/12	calm	48:00:00	8:10:37
	coast	48:00:00	20:33:23
3-4/4/12	calm	48:00:00	32:52:35
	inland	48:00:00	18:51:23
8-12/4/12	calm	96:00:00	36:37:24
	inland	96:00:00	50:05:45
14-15/4/12	calm	48:00:00	13:18:35
	coast	48:00:00	20:09:42
17-18/4/12	calm	48:00:00	25:08:24
	coast	48:00:00	25:31:53
21-22/4/12	calm	48:00:00	8:17:40
	inland	48:00:00	46:34:18
24-25/4/12	calm	48:00:00	11:13:10
	inland	48:00:00	44:34:54
27-28/4/12	calm	48:00:00	20:12:45

6.1.2 Analysis

$PM_{2.5}$ samples were collected on quartz fiber filters (MUNKTELL). Filter diameter was 47 mm for medium volume samplers and 102 mm for high volume sampler.

Details on the determination of ambient concentration of $PM_{2.5}$ are reported in chapter 3.2.1.3. After PM quantification, filters were split in parts for the different chemical

specie determination (Figure 6.2). Medium volume samplers collected simultaneously $PM_{2.5}$ coming from the same direction. The sampled filters were considered as a unique sample and each one was used for different chemical species determination. One of the filters was used for polycyclic aromatic hydrocarbons determination, while the other was split as follow:

1 cm^2 filter punch: OC and EC

1.6 cm diameter filter punch: ions

0.6 cm diameter filter punch: Lvg

Remaining part: metals

High volume filter split instead was:

1/4: polycyclic aromatic hydrocarbons

1 cm^2 filter punch: OC and EC

1.6 cm diameter filter punch: ions

1.6 cm diameter filter punch: Lvg

1/4: metals

The subsamples dimensions were chosen on the basis of expected air concentration of the different chemical species and of the limits of quantifications of the analytical methods.

For the determination of inorganic ions (SO_4^{2-}, NO_3^-, Cl^-, Ca^{2+}, Na^+, NH_4^+, Mg^{2+} and K^+), the filter punches were extracted with 10 ml of bidistilled water, in an ultrasonic bath for 40 min at room temperature. The obtained solution is filtered with polypropylene membrane filters with pore size 0.2 μm (0.2 μm, 25 mm, VWR) and the ions were determined by ionic chromatography as reported in chapter 3.1.2. PAHs, levoglucosan, OC and EC and metals (cadmium, lead, copper, nickel, iron and zinc) extraction and analysis procedures were the same reported in chapter 3.1.2.

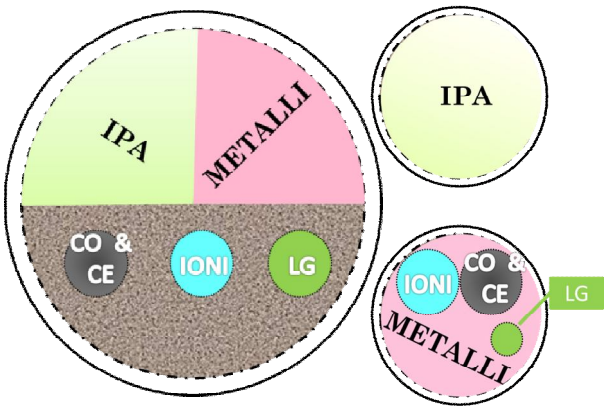

Figure 6.2: Filter split for the different analysis

6.1.3 Quality control

Considerations on trueness of the analysis are reported in chapter 3.1.3.

The precision of the technique has been assessed bythe separate extraction of a sampled filter subsamples (see chapter 3.1.3 and 2.1.4 for more details). RSD for each determined components are reported in Table 6.2.

Tests have been performed to establish the limits of quantification of the method for each determined PM component. While the limit of detection (LoD) can be defined as "*theconcentration which gives an instrument signal significantly different from the 'blank' or 'background' signal*", the limit of quantitation (LoQ) is regarded as "*the lower limit for precise quantitative measurements, as opposed to qualitative detection*". There is still no full agreement on the exact definition of the limit of detection, based on a suitable interpretation of the phrase 'significantly different'. But there is an increasing trend to define the limit of detection as "*the analyte concentration giving a signal equal to the blank signal, y_B, plus three standard deviations of the blank, s_B*"[83] (Equation 9):

$$\text{Limit of detection} = y_B + 3s_B \qquad (9)$$

Similar consideration can be applied to the limit of quantification. Its definition is similar, except for "three", which is commonly substituted by a number included between six and ten[91]. In this work six is used and the LoQ is defined as follow:

$$\text{Limit of quantification} = y_B + 6s_B \qquad (10)$$

For each determined PM component, method quantification limit has been determined by the analysis of four blank filters with the same procedure as samples. Results are reported in Table 6.2. Method LoQ refers to extract concentrations. In this work, it is not possible to have a unique LOQ method for air concentrations. In fact, every sampling had its own length (see Table 6.1) and thus a different sampled air volume. In Table 6.2, instrumental quantification limits and field blank concentrations are also reported. For the most part, field blank values were below the LoQ. For some components, field contamination can be observed, especially for OC, as it generally occurs because of the high volatility of many organic compounds.

Table 6.2: Instrumental quantification limit, method quantification limit and concentration registered in field blank filters.

	RSD (%)[¤]	InstrumentalLoQ	Method LOQ[§]	Field blank 1	Field blank 2	
Na^+	8	0.02	Inst. LoQ	0.03	<inst. LoQ	mg/l
NH_4^+	2	0.02	0.07	<met. LoQ	<met. LoQ	
K^+	8	0.05	Inst. LoQ	<inst. LoQ	<inst. LoQ	
Ca^{2+}	7	0.05	Inst. LoQ	<inst. LoQ	0.07	
Mg^{2+}	10	0.05	Inst. LoQ	<inst. LoQ	<inst. LoQ	
Cl^-	9	0.08	Inst. LoQ	<inst. LoQ	<inst. LoQ	
NO_3^-	1	0.1	Inst. LoQ	<inst. LoQ	<inst. LoQ	
SO_4^{2-}	2	0.1	Inst. LoQ	<inst. LoQ	<inst. LoQ	
Lvg	5	0.005	0.046	<met. LoQ	<met. LoQ	
Flu	7	<0.10	4.08	<inst. LoQ	<met. LoQ	µg/l
Pir	8	0.25	7.66	<inst. LoQ	<met. LoQ	
B(a)A	6	<0.10	1.48	<met. LoQ	<met. LoQ	
Cri	5	<0.10	2.27	<met. LoQ	<met. LoQ	
B(b)F	5	0.50	1.53	<inst. LoQ	<inst. LoQ	
B(k)F	5	<0.10	1.33	<met. LoQ	<met. LoQ	
B(a)P	9	<0.10	1.28	<met. LoQ	<met. LoQ	
D(a,h)A	5	0.50	2.19	<met. LoQ	<inst. LoQ	
B(g,h,i)P	4	0.25	2.58	<met. LoQ	<inst. LoQ	
I(1,2,3)P	4	<0.10	2.54	<inst. LoQ	<met. LoQ	
Cd	7	0.025[*]	Inst. LoQ	<inst. LoQ	<inst. LoQ	
Pb	6	1.00[*]	Inst. LoQ	2.26	<inst. LoQ	
Cu	6	0.25[*]	1.09	<met. LoQ	1.10	
Ni	11	1.00[*]	Inst. LoQ	1.07	1.00	
Fe	4	1.00[*]	51.90	<met. LoQ	<met. LoQ	
Zn	14	25[#]	Inst. LoQ	<inst. LoQ	<inst. LoQ	
OC	10	0.2	Inst. LoQ	3.4	4.0	µg/cm^2
EC	20	0.2	Inst. LoQ	<inst. LoQ	<inst. LoQ	

[§] For many components, blank filter concentration was below the instrumental detection limit. In these cases, the method detection limit is equal to the instrumental detection limit.

[*] Graphite furnace AAS

[#] Flame AAS

[¤] Mg^+ concentration resulted<LoQ in the precision test. Since Mg^+ concentration is usually <LoQ also in samples (see Appendix IV), an arbitrary but presumable value has been chosen. OC and EC values are those usually used in similar studies

6.1.4 Positive Matrix Factorization (PMF)

The unit of measurement has been chosen in order to have data values not extremely small or extremely large. For this reason, air concentrations of metals and PAHs were expressed in ng/m^3, while air concentrations of ions, Lvg, OC and EC in μg/m^3.Lvg and PAHs are organic compounds, therefore their carbon contents are present twice in the dataset (in OC and in Lvg or PAHs concentration). This leads the variables not to be independent. Therefore for each sample, the Lvg and PAHs carbon contents has been subtracted to the total OC amount.

Standard deviations (s_{ij}) was calculated with EM=-12 option (Equation 3, chapter 4.2). In this study C1 was specified individually for each measurement (standard deviations matrix). For each value x_{ij}, the standard deviation was computed as suggested by Hopke[10] (Equation 11):

$$C1 = \frac{RSD_j x_{ij}}{100} + \frac{LoQ_{ijmet.}}{3} \quad (11)$$

the first term of the equation was considered as the analytical uncertainty.RSD values are reported in Table 6.2, while $LoQ_{met.}$ for air concentrationshave been calculated individually for each sample by using the method quantification limit reported in Table 6.2 and the sampled volume.For OC, C1 has been calculated according to propagation of systematic error rules. The corrected C1 for OC ($C1_{OC_{cor}}$) therefore was

$$C1_{OC_{cor}} = C1_{OC} + C1_{C_{Lvg}} + C1_{c_{PAHS}} \quad (12)$$

Where

$$C1_{C_{Lvg}} = \frac{C1_{Lvg} 12(n°C)}{MW_{Lvg}} \quad (13)$$

And

$$C1_{C_{PAH}} = \frac{C1_{PAH}12(n°C)}{MW_{PAH}} \quad (14)$$

Where

n° C= number of carbon atoms in the molecule

MW=molecular weight

C2 was =0, as usually used[70], while for C3, different values between 0.00 and 0.20 were tested[69,79].

The Robust mode, together with the value of four times the S.D. of the species to define outliers, was used to minimize the distortion of dataset by the outliers[80]. Since there are some missing data and a lot of data below the detection limit, the optional parameter "BDLneg r1 r2" was used. As suggested by Paatero[70], r2=10 was used.

The appropriate number of factors extracted and the value of C3 were then determined based on the satisfying of most of the following criteria (the first four criteria were based on Lee et al.[73]and Chan et al.[80]:

- Value of Q close to n x m – p x m – p x n (i.e. the degree of freedom of the analysis).
- R90 (the 90 percentile of the scaled residuals, r_{ij}) is within ±2. That is, most of the residuals are within 2.
- A sharp drop in IM and/or IS
- A significant increase in the largest rotmat element.
- Reasonable estimated source profiles

Three to 12 different factors were tested, but only six factors and C3=0.09 were found to obey all the required constraints and resulted in physically meaningful solution (see Figure 6.3 for IM, IS and ROT values for C3=0.09). The optimal Q-value obtained with this model was 1222, which compares reasonably well with the theoretical value of 1098 for the six factor model. R90 is within ±2. Specifically, 97% of the residuals are within ±2. Six factors explained >75% of the variations in most species. The rotational state of

the result has been controlled by the "peaking parameter" FPEAK. The solution with FPEAK=0 (no rotation) resulted in the most physically meaningful solution.

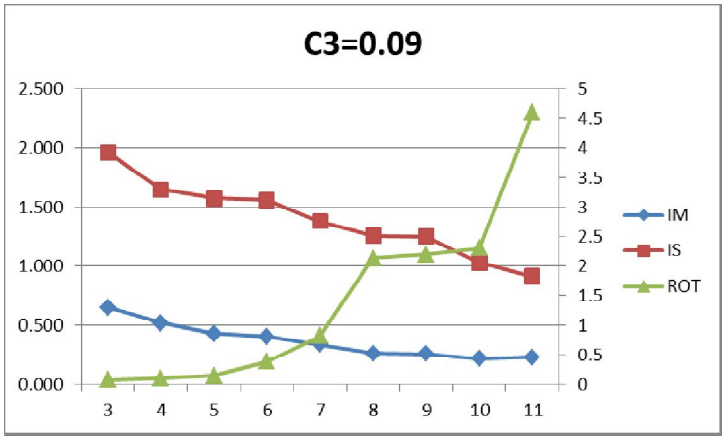

Figure 6.3: Determination of the number of factors, using C1=0.09

6.1.5 Multi Linear Regression (MLR)

To quantitatively estimate the mass contributions of the six resolved sources, the fine PM mass was regressed against the factor scores using MLR. The constant of the linear regression was assumed to be zero. This regression process also provided an additional test for the PMF model and the appropriate number of factors that had been chosen for the analysis. An unrealistic number of factors for the PMF model very often resulted in negative values for the MLR coefficients[103]. For the 6-factor solution, the obtained regression coefficients were all positive values. P-values lower than 0.05 for four of the six factors, as R-squared value, indicate statistically that the observed PM mass concentrations were represented quite well by the resolved six factors. Biomass combustion factor shows a high standard deviation value of the MLR coefficient, therefore the results for this factor should be misleading. The reconstructed mass concentrations of the 60 samples from the factor scores and the regression coefficients versus the observed fine PM mass concentrations are shown in Figure 6.4. A summary of the regression results is shown in Table 6.3.

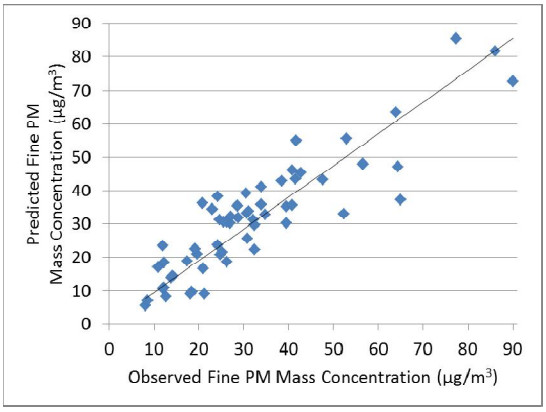

Figure 6.4: Predicted PM mass concentrations plotted against the observed values.

Table 6.3: Multiple regression analysis of fine particles.

Source	**MLR coefficients**	**MLR coefficient Std. Dev.**	**P value**
Natural gas home appliances	3	2	0.082
Motor vehicle	19	3	0.000
Long-range transport	5	2	0.014
Biomass combustion	3	4	0.451
Industry	5	2	0.007
Secondary nitrate	19	2	0.000
R-Squared	0.950		
R-Squared (adjusted for d.f.)	0.927		
Standard Error of coefficients	8.73		

6.2 RESULTS AND DISCUSSION

6.2.1 Air concentrations

A complete overview of the obtained results is reported in Appendix IV, while in Figure 6.5 geometric means for $PM_{2.5}$ and its determined components are reported. Samples have been split in order to compare air masses coming from the inland, from the coast and connected to calm conditions. $PM_{2.5}$ mean concentration is above the law limit. The samples have been mainly collected in cold months and therefore they do not represent a

mean year, where the summer months contribute to reduce $PM_{2.5}$ mean concentration. Nevertheless the registered values are quite high and the study area proves to be subject to a significant pollutant load and worthwhile to be monitored. As far as other regulated pollutants, they are well below law limits.

Main PM components are those connected to secondary particulate matter: nitrates, ammonium, sulfates and OC. This last can have also a primary origin.EC contribution is also important. Generally, contaminant concentrations are similar to what is found in other suburban sites and markedly lower than urban concentrations[42,43,46,52,104,105,106,107,108,109,110]. Among the determined components, OC is the only one which shows a concentration which can be considered quite high in comparison with what is general found in other sites[42,46,47,111,112,113,114]. Specifically, OC concentration is particularly high in samples connected with calm conditions (Figure 6.6). The higher concentrations are registered during the first samplings, i.e. in November and in December. In 2012 concentrations decrease, nevertheless they continue to be particularly high.

As expected, $PM_{2.5}$ concentration is higher in calm condition samples.Windsgenerally led to a greater atmospheric mixing, which tends to scatter pollutants and thus to decrease their air concentration. OC and PAHs show the same trend.

Ammonium, EC, potassium and iron concentration is higher in air masses coming from the inland and can be thus somehow connected with incinerator or motorway activity.

Nevertheless the variability is very high and it is difficult to come to definitive and proved conclusions. Therefore a deeper data analysis results essential in order to have information on the effect of the sources impacting on the area.

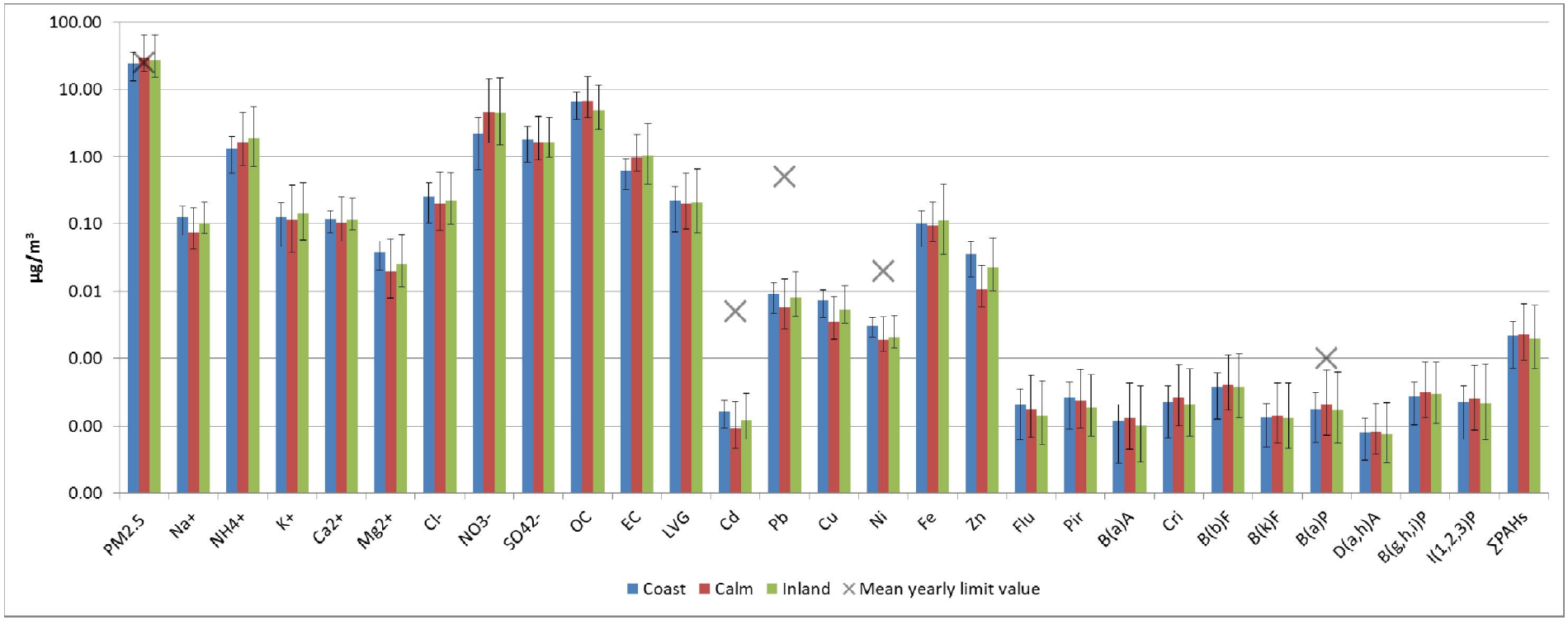

Figure 6.5: Air concentration geometric means of $PM_{2.5}$ and its determined components for air masses coming from the inland, the coast and sampled in calm conditions. The bars represent the standard deviation and are therefore an index of data dispersion.

* *When the component concentration was below the limit of quantification, air concentration was calculated using ½ DL, as suggested by Italian National Institute of Health (ISS)*[91]

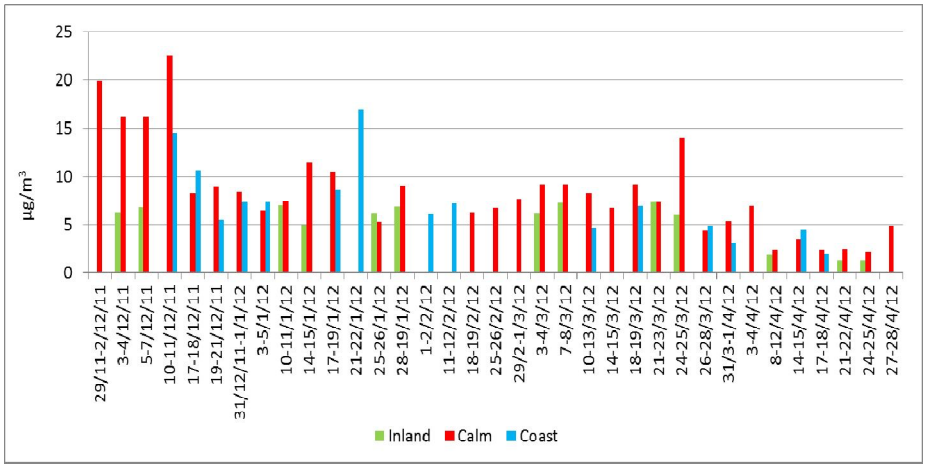

Figure 6.6: OC concentration in inland, coast and calm samples.

6.2.2 Source profile

The overall mass concentration profiles of the six factors are shown in Figures from 6.7 to 6.12. First factor consists mainly of OC and sulfate; it is composed of 41% the first and 31% the latter. Sulfate formation and transport has a regional nature, therefore this factor can be identified as long-range transport[115,116]. Sulfate is secondary material, since is due to the oxidation of SO_2, and it is usually associated with other secondary material, as OC[117]. By considering the molar ratio NH_4^+/SO_4^{2-}, sulfate is in strong excess. This can be due to the evaporation of ammonium during sample analysis[116] and to other origin of sulfate, e. g. marine spray. Indeed this factor is also composed of sodium (4%), magnesium (2%), calcium (4%), chloride (3%) and iron (3%). This suggests that in addition to secondary material, the long-range transport aerosol was also composed of marine spray and resuspended soil[115]. Sodium origin is very useful in order to evaluate sea fraction contribution, while calcium is one of the main constituents of soil.

The second factor can be associated to secondary nitrate factor. This factor is represented by high concentrations of nitrate and ammonium, 54% of both was loaded in this factor. Sulfate (53%) and potassium (40%) and a small amount of chloride (17%) and OC (20%) were also associated with this factor. This can also be explained by the secondary aerosol formation process as previously mentioned. Molar ratio of ammonium to nitrate was 1.7. Considering the mixed sulfate in this factor and the uncertainty of the PMF model, the nitrate is probably present as ammonium nitrate. It is due to the conversion of NOx,

emitted both by vehicular traffic and by other combustion processes. The presence of potassium, marker of biomass combustion, suggests that NOx are emitted also from this source. Other PMF results show a similar behavior, with the presence of potassium in secondary nitrate factor[116,118].

The third factor is biomass burning and it is mainly characterized by levoglucosan, nearly all (85%) was loaded into this factor. It is probably related to local residential and commercial wood burning and local agricultural burning. Other major contributors in the chemical profile are NO_3^-, OC and EC. The presence of K (another tracer for biomass combustion) and Cl in the factor profile confirms the assignment of the wood burning source to this factor[119]. Indeed a large fraction (31%) of potassium and chlorine (64%) were associated with the factor. Pb and PAH, especially the heaviest, can also be markers of wood smoke, as demonstrated in our previous study (chapter 3). 21% of lead was associated with this factor, while between the 35 and the 55% of PAHs were represented by this factor. Because of the high contribution due to secondary components (e. g. NO_3^-), the factor represents both the wood burning primary and secondary emission[119]. PAHs diagnostic ratios are frequently employed to identify the origin of PAHs in ambient air[120,121]. Many studies[109,120,121,122] agreed in two wood combustion diagnostic ratios: I(1,2,3)P/(I(1,2,3)P+B(g,h,i)P)=0.62 and B(a)A/(B(a)A+Cri)=0.43. The values of the ratio in this factor are 0.57 for the first and 0.42 for the latter. These results confirm the above established attribution to biomass combustion for this factor.

51% of Flu, 44% of Pir, 54% of Zn and 22% of Fe were associated with the fourth factor. Flu and Pir are markers of several emission sources: diesel emission, wood combustion, coal combustion, natural gas, incineration process, oil burning and petrol powered vehicles[41,110,123,124,125,126]. Nevertheless diesel emission is characterized also by other markers, such as EC, B(b)F and B(k)F, which are not well represented by this factor[110,123]. Wood combustion should have a higher contribution of B(a)P[110]. In addition to this, our previous study demonstrated that Flu and Pir are the less abundant PAHs during a bonfire event. Finally Lvg is not represented by this factor. This factor unlikely represents petrol vehicles, since B(g,h,i)P is the best marker for this source[123], but it is represented only for the 16% by this factor. By considering the source profile, coal and natural gas combustion should be good candidates, since the high contribution also of B(a)A and Cri[110,123,125,127]. Coal combustion source is not present in the study area, while natural gas is the most

spread fuel for domestic heating. Considering that emission inventories for the area show that the emissions of non-industrial sources (i.e. hot water heating, gas and oil heaters, fireplace and cookers) account about 70% of total PAHs emissions[128], this factor can be attributed to emissions from natural gas home appliances[129], even if there are no evidence that correlate Zn, which as above mentioned is represented for the 54% by this factor, with this emission source. Incinerator emissions could also be a good candidate for this factor. Fe and Zn in $PM_{2.5}$ are good markers of incineration process[94,96,130], even if they could be emitted also by vehicle exhaust[131,132]. Factor scores could definitively assess the attribution of this factor to natural gas combustion or incinerator.

The most of OC (41%) and EC (58%) are loaded in the fifth factor. EC is a well-known marker of vehicular traffic and the primary organic aerosol is formed during combustion process, therefore it is present in vehicular exhausts. 51% of Ca^{+}, the main road dust component determined, 41% of Cd and 20% of Ni, elements that can be ascribed to fossil fuel combustion[60,61,62,63,64] are loaded in the factor. This confirms the attribution to motor vehicle emissions[116,118]. The factor is composed of 63% OC, 19% NO_3^- and 14% EC. The strong excess of OC compared to EC and the presence of nitrate indicate that this factor represents also secondary traffic emissions[119]. PAHs are also well represented by this factor; among them, B(b)F (35%), B(k)F (32%) and B(g,h,i)P (37%) show the greatest loadings. B(b)F and B(g,h,i)P are components of fossil fuels and a portion of them are associated with their combustion[133].

The bulk of the sixth factor (77%) is composed of OC, but its peculiar characteristic is that most of the Cd, Pb, Cu, Ni, Fe and Zn masses are attributed to this factor (30%, 43%, 30%, 24%, 16% and 46%, respectively). These elements are quite common in a number of source categories, including vehicles, waste incinerators, soil dust, etc. This factor explains most of the Zn and Pb which are incinerator markers[88,94,134,135]; furthermore the total factor profile is similar to what is reported in Ogulei[96] and defined as waste incinerator source. The Zn/Pb ratio was equal to 4.9 for this factor which is about 3 times higher than the 1.8 ratio reported for municipal incinerator emissions[135]. Nevertheless this ratio represents old emission measurements, before Pb reductions in many products[136]. In general a factor with high mass fractions of Zn, Fe, and Pb likely represent a general industrial source[116].

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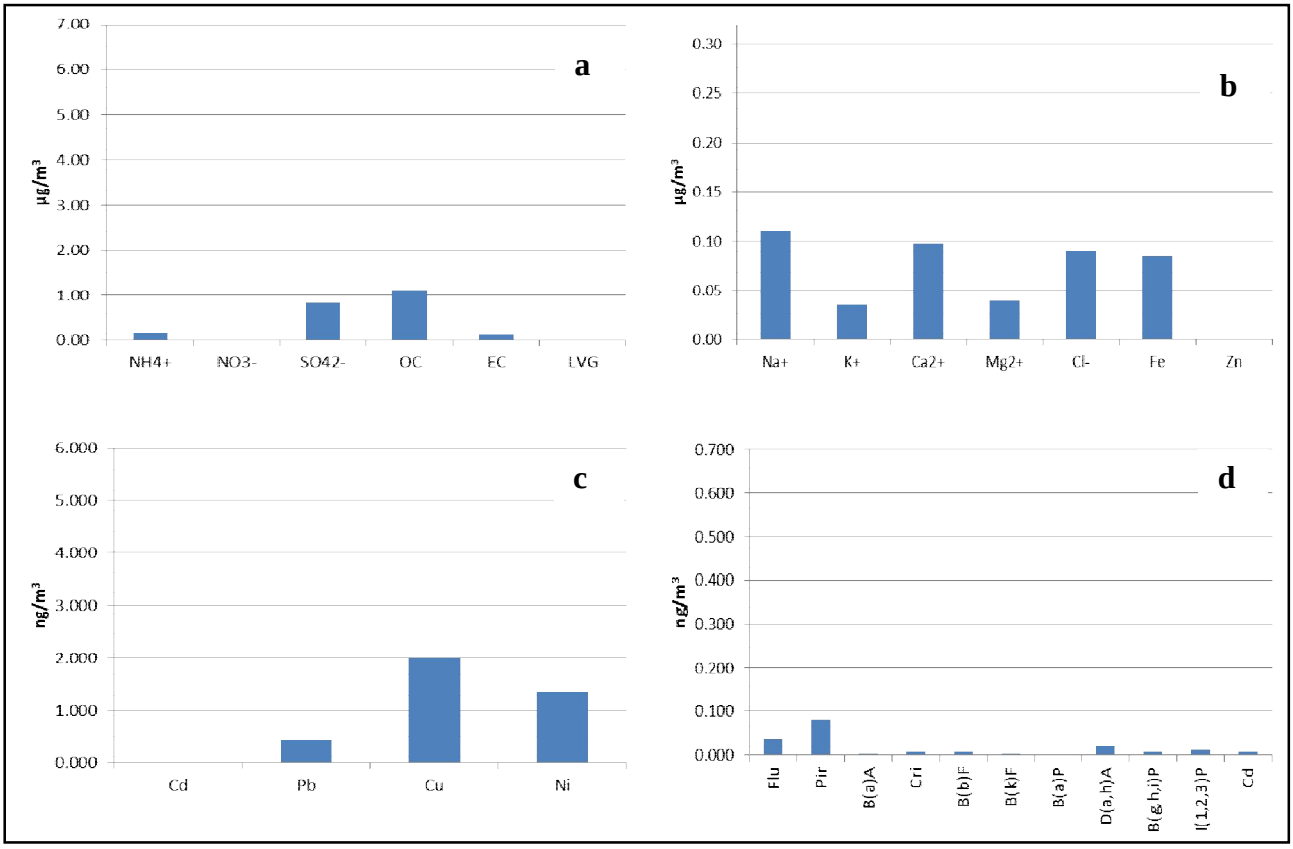

Figure 6.7: Factor1 in mass concentration. The determined components are reported in 4 charts, depending on their concentration. In chart a and b mass concentration is expressed in µg/m^3, in chart c and d in ng/m^3.

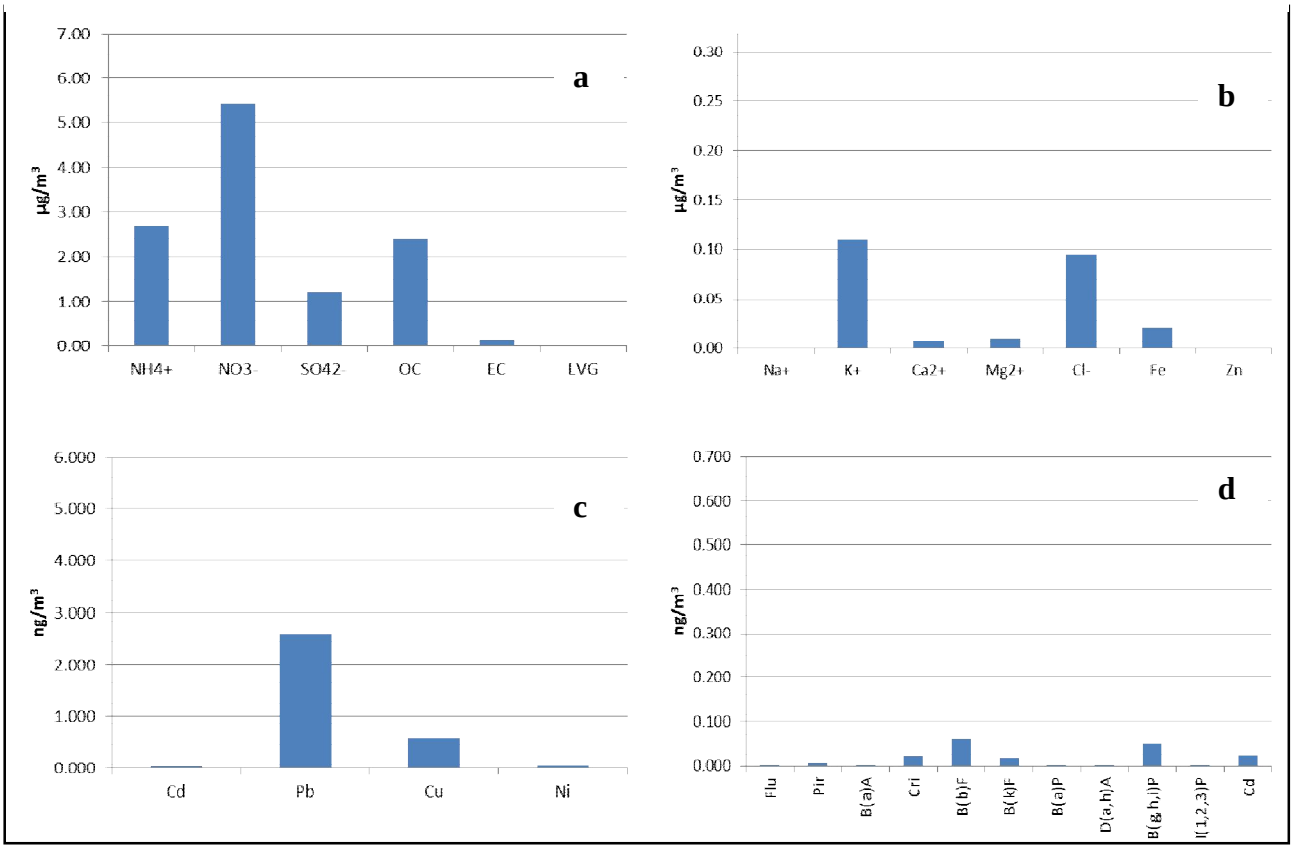

Figure 6.8: Factor 2 in mass concentration. The determined components are reported in 4 charts, depending on their concentration. In chart a and b mass concentration is expressed in µg/m^3, in chart c and d in ng/m^3.

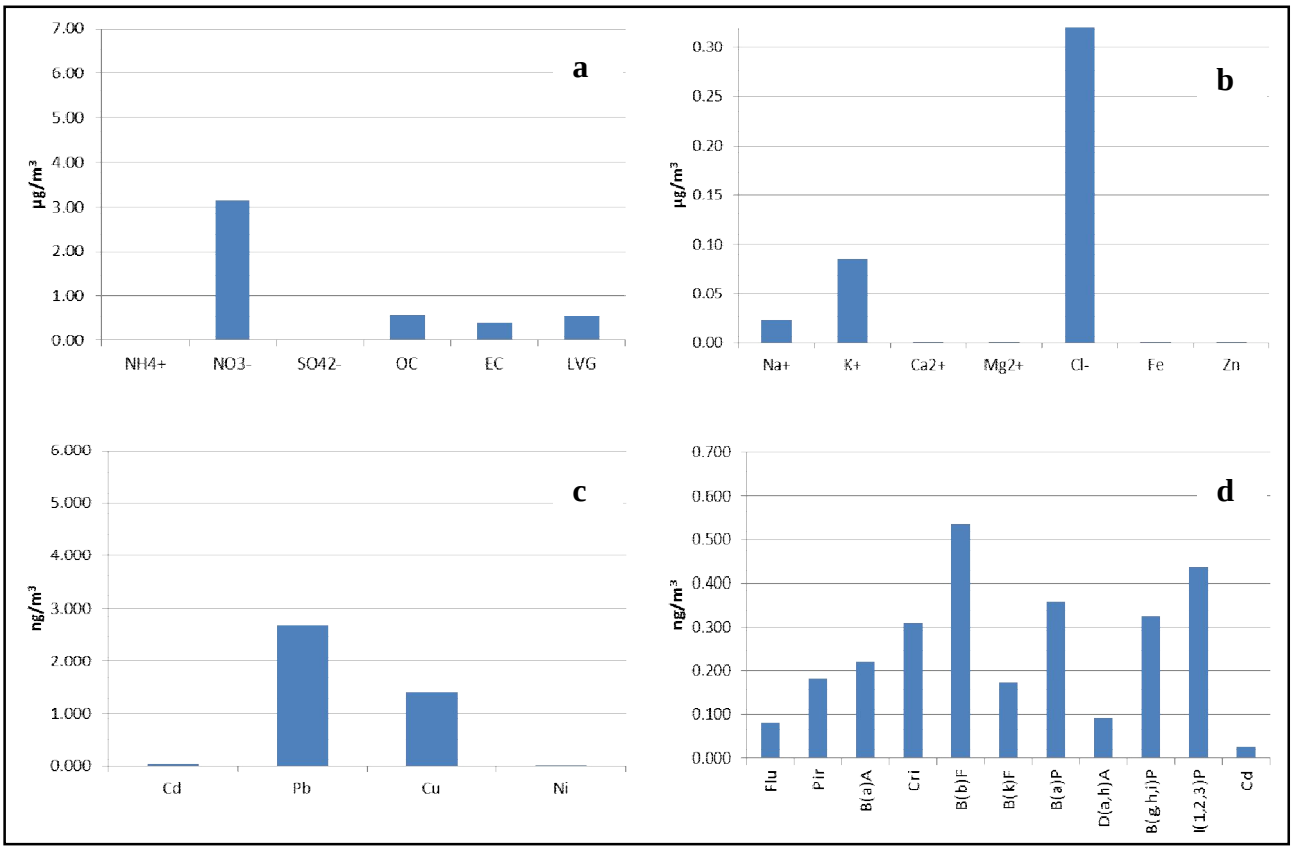

Figure 6.9: Factor 3 in mass concentration. The determined components are reported in 4 charts, depending on their concentration. In chart a and b mass concentration is expressed in µg/m^3, in chart c and d in ng/m^3.

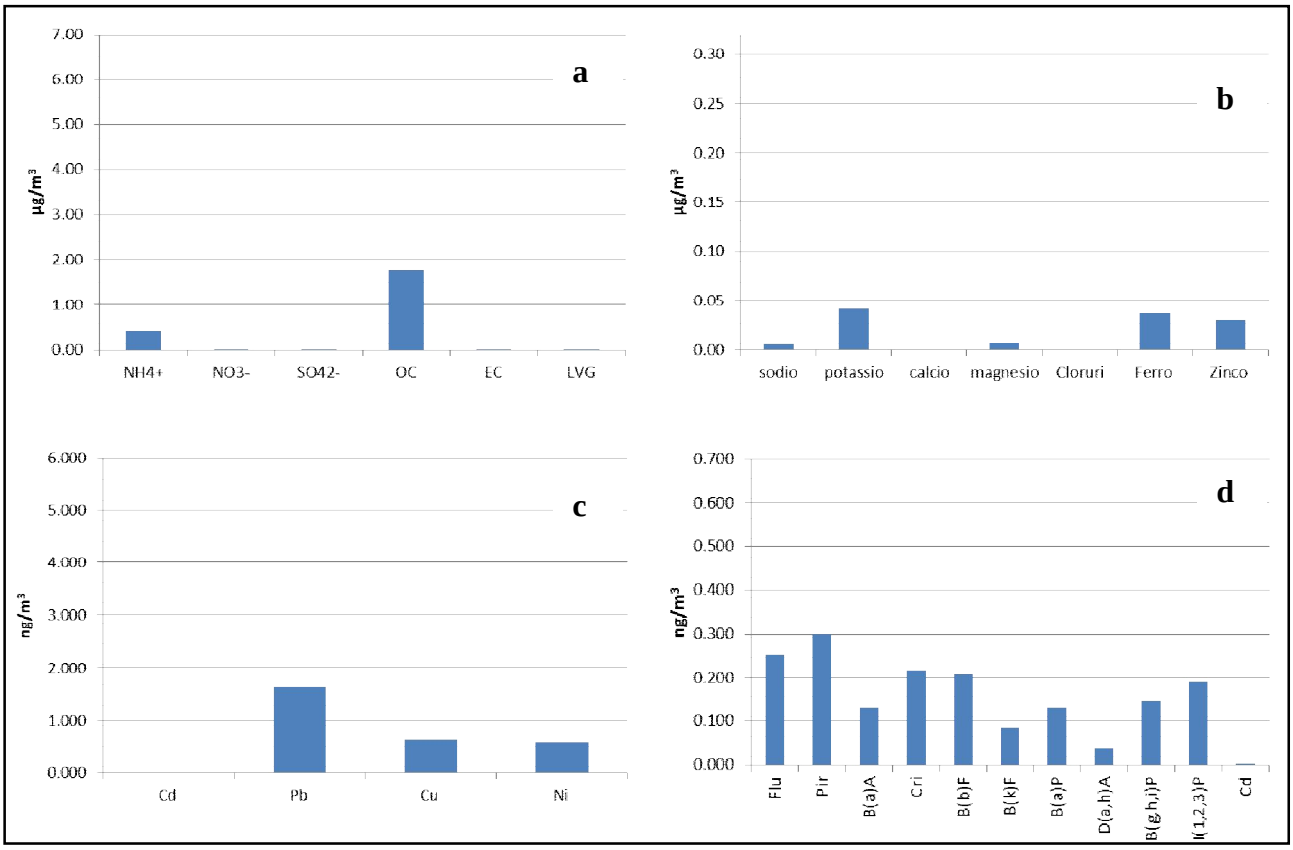

Figure 6.10: Factor 4 in mass concentration. The determined components are reported in 4 charts, depending on their concentration. In chart a and b mass concentration is expressed in µg/m^3, in chart c and d in ng/m^3.

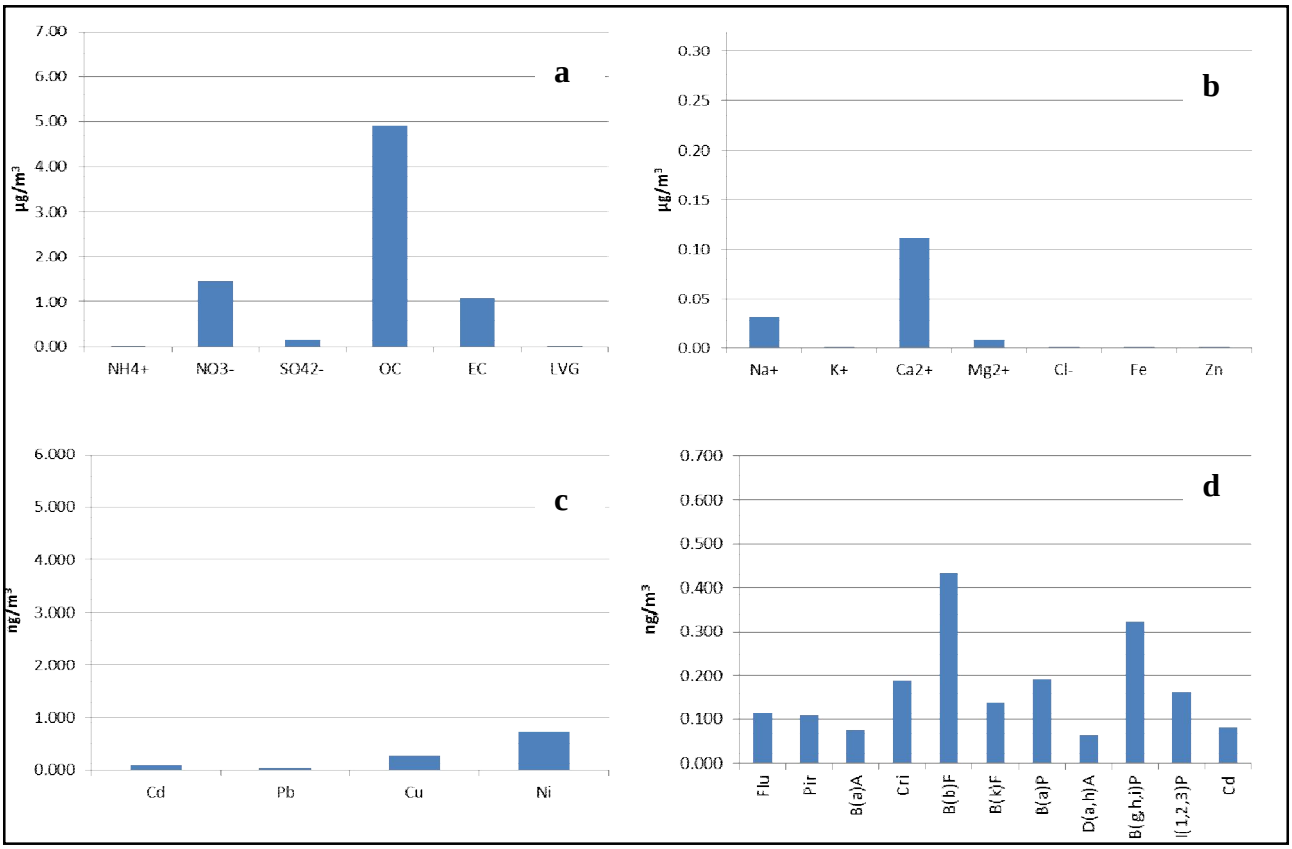

Figure 6.11: Factor 5 in mass concentration. The determined components are reported in 4 charts, depending on their concentration. In chart a and b mass concentration is expressed in µg/m^3, in chart c and d in ng/m^3.

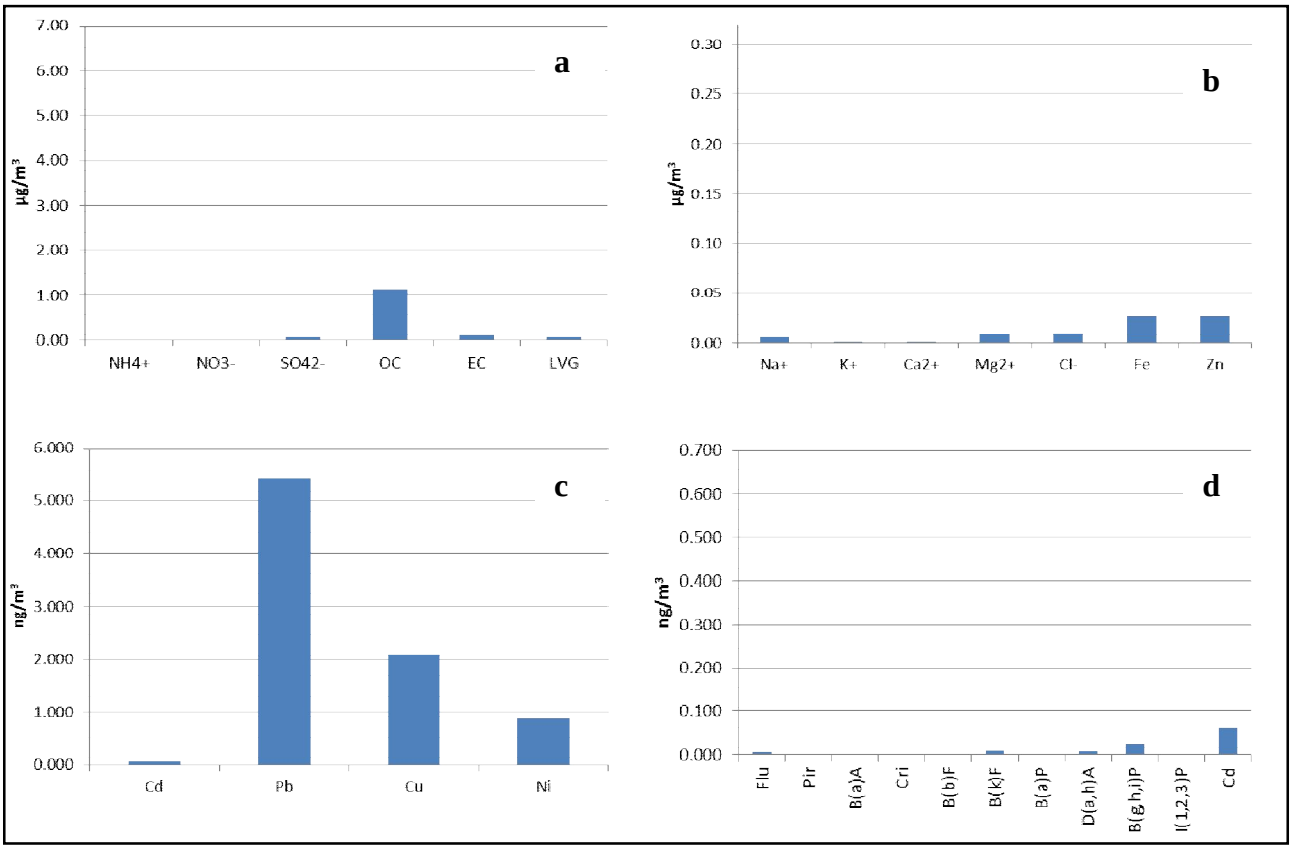

Figure 6.12: Factor 6 in mass concentration. The determined components are reported in 4 charts, depending on their concentration. In chart a and b mass concentration is expressed in µg/m^3, in chart c and d in ng/m^3.

6.2.3 Factor contribution and comparison among the air masses

The objectives of this study are both to determine the sources affecting the area and to assess which is the prevailing origin direction of the input sources. Therefore, the study aim is to identify which is the pollutant load due to local sources compared to long-range transport.

The contribution due to calm conditions, to the air masses coming from the coast and from the inland to the total pollutant load should be assessed. By considering the input and the effective sampling time, the per cent time each of the three conditions is present in the area during the whole period was determined. The 30% of the total time was characterized by calm conditions, the 42% by air masses coming from the inland and 28% by air masses coming to the coast.

To quantitatively estimate the mass contributions of the six resolved sources, the fine PM mass was regressed against the factor scores using MLR. Then the median contribution of the six sources to the total pollutant amount was considered, by giving a different load to the three conditions on the basis of the temporal per cent contribution. The median contribution of the six sources to calm conditions, to the air masses coming from the coast, to the air masses coming from the inland was also assessed (Figure 6.13).

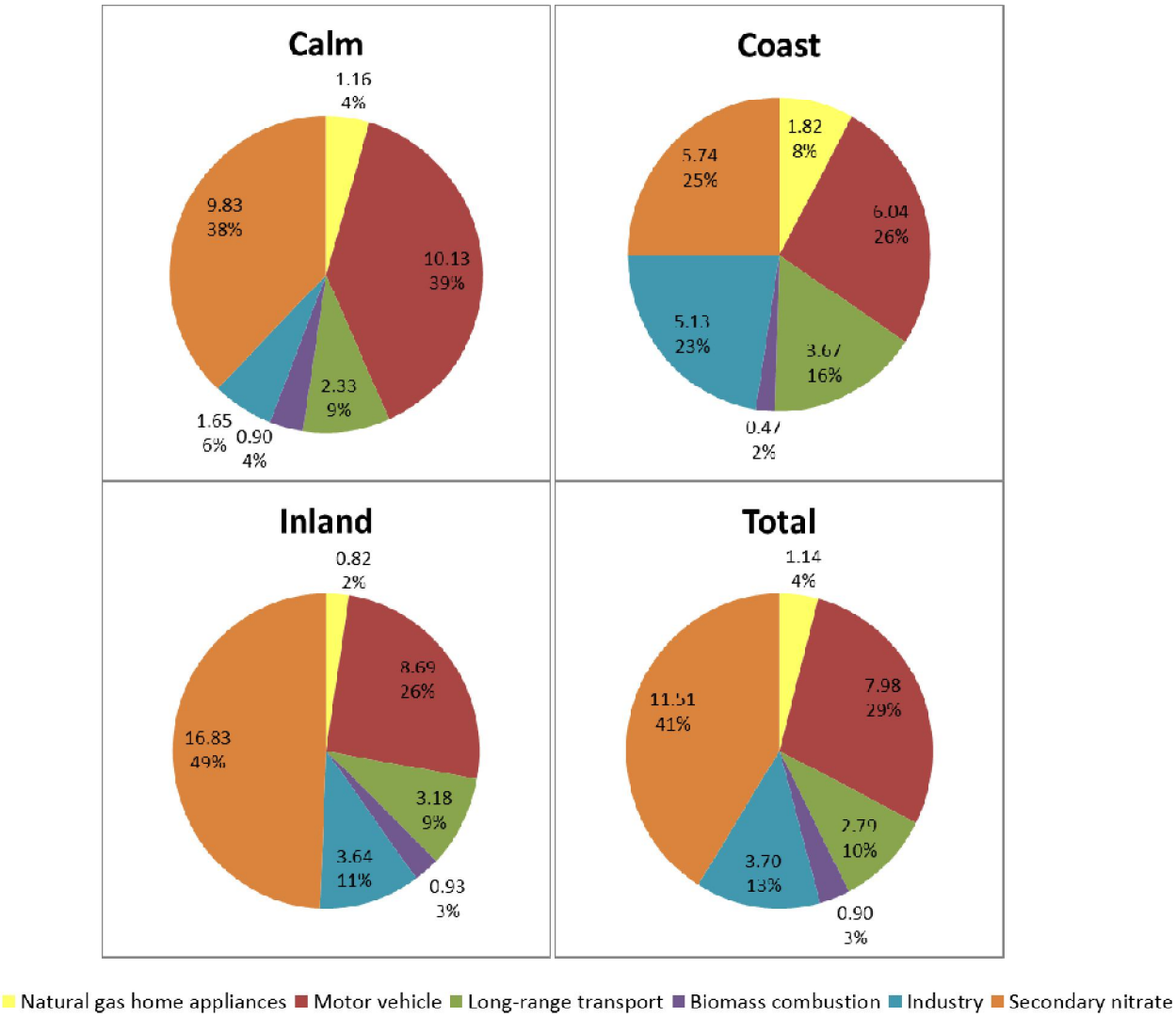

Figure 6.13:Average factor contribution (percentage and concentration in µg/m^3) of each factor to PM for calm conditions, inland air masses, coastal air masses and total

The main source of $PM_{2.5}$ in the area is secondary nitrate, its contribution to the total $PM_{2.5}$ was 41%. The major contribute is due to the air masses coming from the inland, the median value of the source contribution in these air masses is almost three times higher than in the coastal air masses, where secondary nitrate is not even the main source. This behavior could suggest that this source is somehow correlated with the incinerator. However this is not a primary source and the distance between the sampling site and the incinerator is too short to justify the conversion of NOx to nitrates. Therefore this source should have a more distant origin and be due to regional contributions.

Motor vehicle emission source contributes 29%. In this case the major contribution is due to calm conditions. In these air masses, as in coastal, this factor and secondary nitrates factor contribution is almost the same. Only in the inland air masses secondary nitrates

contribution is markedly higher and this supports an inland origin for this source. Since the highest contribution for motor vehicle emission is due to calm conditions, this source has likely a prevalent local origin.

The industry source contributes 13%. The major contribute is due to the air masses coming from the coast. This result confirms the attribution to this factor to a general industrial source rather than the incinerator. More generally this source can be therefore related to industry. Since the low contribution in calm condition air masses, this source is not likely strictly local.

Long range transport counts for 10%. As expected, the contribution of calm conditions (i.e. of local sources) is the lowest, while the main contribution is due to coastal air masses, since this factor is also composed of marine spray.

It was not possible to definitely ascribe fourth factor only on the basis of source profile; incinerator emission and natural gas home appliances are the most probable candidates. This factor contributes for the 4% to the total $PM_{2.5;}$ the main contribution is due to coastal air masses, while inland air masses contribution is the lowest. Therefore the source is difficultly ascribable to the incinerator but is more likely natural gas home appliances. This is confirmed also by the significant inverse correlation ($R=-0.70$, p value<0.001) between temperature and the factor.

Biomass combustion is the factor which presents MLR results less significant, since the high p-value (see chapter 6.1.5). Nevertheless its contribution to the total $PM_{2.5}$ is very low, 2% and this data affects little the overall results. The main contribution is made by calm condition and inland air masses. Therefore the source origin is local and stronger from the inland. This kind of combustion, which is used also for domestic heating, should be more spread in the rural area than in the town. The correlation of this source to domestic heating is confirmed by the significant inverse correlation ($R=-0.48$, p value<0.001) between temperature and the factor.

In Figure 6.14 the temporal trends of the source contribution and of $PM_{2.5}$ are reported. As expected, thecontribution of sources related to domestic heating, e.g. natural gas home appliances and biomass combustion, is higher in winter and decreases at the approach of spring. Secondary nitrate contribution is similar throughout the whole sampling period, only April samples show a lower contribution. This is consistent with $PM_{2.5}$

concentration, which decreases on April. Also motor vehicle emission factor concentration in April is lower, while long-range transport factor concentration increases as spring approaches; this is due to the increase in photochemistry that favors formation of particulate sulfate[117]. The per cent contribution to PM is particularly high during the last sampling days and during samplings characterized by snowfall (1^{st} -2^{nd} February and 11^{th}-12^{th} February. Industry emission is the only source which shows a different temporal trend between calm condition air masses and coastal and inland ones. While in calm condition air masses the contribution is similar all period long, in inland and coastal air masses the contribution on April is lower.

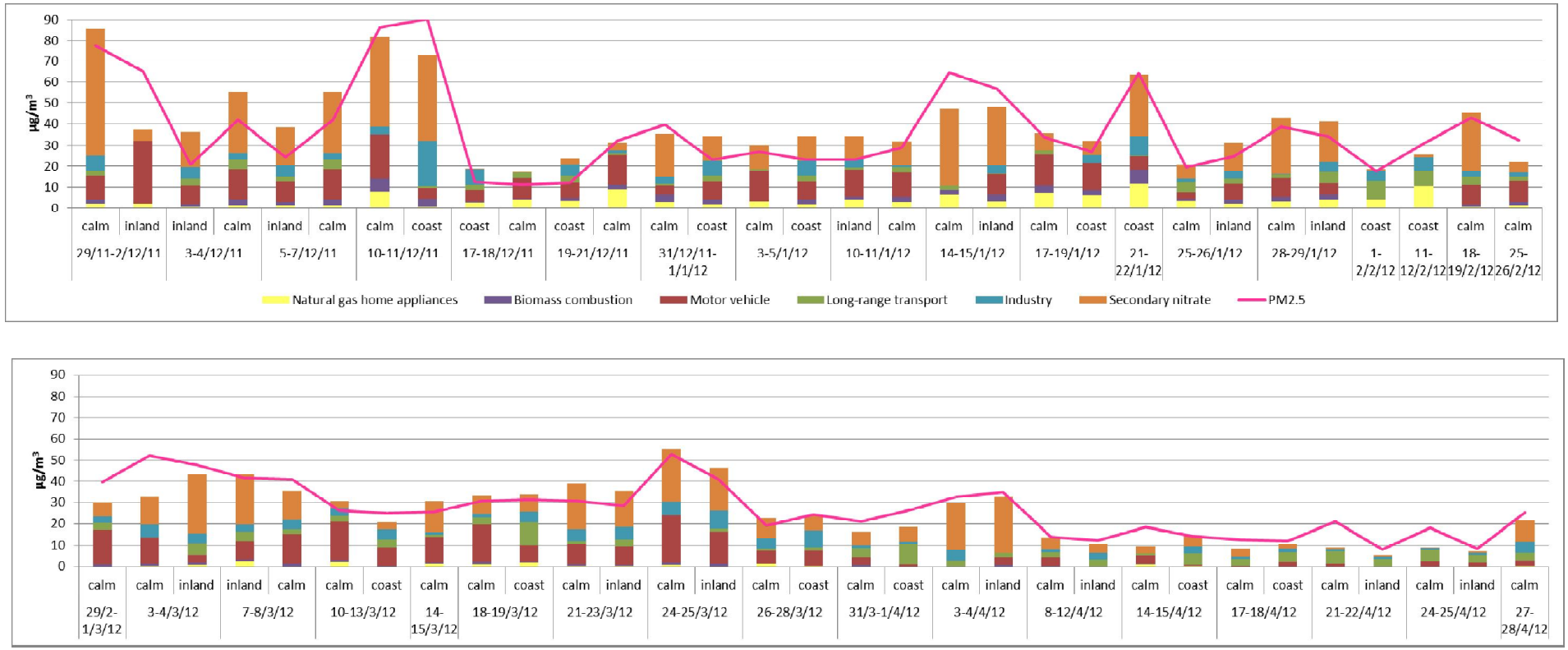

Figure 6.14: Temporal trend of factor contribution to$PM_{2.5}$ and of $PM_{2.5}$

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Among the components analyzed, heavy metals and PAHs are those which create the greatest concern, due to their toxicity; metals are also persistent in the environment. Therefore it is important to assess which are the main sources of these constituents (Table 6.4) in the area.This assessment was performed by the analysis of factor scores multiplied for the concentration of the constituent in the factor.

The main PAHs source in the area is vehicular traffic. Up to 67% of PAHs is due to this source. This high contribution can be found in all the air masses,64% minimum of PAHs is ascribable to this source. Other appreciable PAHs sources are due to natural gas home appliances, biomass combustion and secondary nitrate, which contribute for about 10% each.

For what concerns metals, vehicular traffic is also the main sources of Cd and Ni, which is consistent with their principal source, i.e. fossil fuel combustion. Industry is an important source of metals in the area, the principal for zinc and copper. Secondary nitrate is also an important source of metals. Even if metal concentration in the source profile is very low, the high impact that the source has on the area justifies the result. Secondary particulate can form after condensation on pre-existing particulate which can contain these metals.

Table 6.4: Per cent average contribution of each factor to metals and PAHs in $PM_{2.5}$.

%	Natural gas home appliances	Motor vehicle	Long-range transport	Biomass combustion	Industry	Secondary nitrate
PAHs	9	68	2	11	1	10
Cadmium	0	55	2	2	19	22
Lead	3	0	2	4	36	54
Copper	3	9	23	5	32	28
Nickel	5	41	27	0	23	3
Iron	7	0	38	0	16	38
Zinc	26	0	0	0	73	0

6.3 CONCLUSION

$PM_{2.5}$ air concentration in the study area is quite high; mean value is above law limits, while other regulated pollutants are far below law limits. OC concentration is quite high when compared to other studies, especially in calm condition samples. Mean values for $PM_{2.5}$ and its determined components show a daily high variability.

PMF analysis indicates that six main sources affect the area: natural gas home appliances, motor vehicle, long-range transport, biomass combustion, industry and secondary nitrate. The connection of factor temporal trends with other parameters (i.e. temperature, $PM_{2.5}$ concentration and photochemical processes) confirms factor attributions.

The main source of $PM_{2.5}$ in the area is secondary nitrate. This should be mainly due to regional contributions, since the secondary nature of the source itself and the higher concentration registered in inland air masses. A motor vehicle emission source contribution is also important. This source likely has a prevalent local origin, its concentration is higher in samples connected with calm conditions. The most toxic determined components, i.e. PAHs, Cd, Pb and Ni, are mainly due to vehicular traffic.

Even if vehicular traffic is not the main source in the study area, its prevalent local origin and its contribution of toxic component make it the source of greatest concern for the study area and thus the one it is worthy to operate on the most, at least in order to reduce metals and PAHs concentration.

The deeper data analysis applied resulted essential in order to appreciate some differences which could not be determined by a general qualitative analysis of data.

This higher temporal resolved study confirms that incinerator contribution in the study area is negligible compared to other sources.

7 Positive matrix factorization of high time resolution aerosol data in urban area

7.1 EXPERIMENTAL METHODS

7.1.1 Sampling and analysis

Sampling and analysis was conducted by the Air Quality Laboratory (AIR) of the Technical Unit for Environmental Assessment Models, Methods and Technologies (UTVALAMB) of Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA).

Briefly the sampling campaign wasundertaken at ENEA - Bologna Research Centre (44°31'30",63 N11°20'40",92 E) during winter 2011. The site is located in a densely populated residential area, close to a road and about 1 Km far away from one of the most important and congested motorway junction in Northern Italy. (Figure 7.1).

Online hourly measurements of Organic Carbon (OC) and Elemental carbon (EC) were performed with a semi-continuous OC/EC analyzer (Model-4 Field analyzer, Sunset Lab.) using the EUSAAR 2 thermal protocol. Water soluble inorganic ions (Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+) hourly measurements were performed with an aerosol ion monitor (AIM, URG 9000D). Both were determined in $PM_{2.5}$.$PM_{2.5}$ mass concentrations were measured with a dust monitoring system, Mobile Enviro Check GRIMM EDM107.The instruments were located inside a climate-controlled container. More details on the instruments are reported in Malaguti et al[137].

Figure 7.1: Studied area on a large-scale map (a, b) and a local map(c) and theclimate-controlled container

7.1.2 Positive Matrix Factorization (PMF)

Two analysis were performed, the first one by considering only OC, EC and soluble ions as variables, the second by adding also PM_1, $PM2.5_{-1}$ and $PM_{10-2.5}$. Since only some components of PM were determined, it was not possible to obtain mass closure. The inclusion of the measured fine particle mass concentrations as an independent variable in the PMF modeling allows to directly obtain the mass apportionment without the usual multilinear regression[138,139,140]. The first analysis had the aim to resolve the source profile of the sources affecting the area while the second has the only aim to obtain the mass apportionment, while source profiles can be somehow falsified by the presence of PM as variable.

Standard deviations (s_{ij}) was calculated with EM=-12 option (Equation 3, chapter 4.2). In this study C1 was specified individually for each measurement (standard deviations matrix). For OC and EC, the standard deviation values provided by the instrument were used; when they were missing, they have been replaced by the mean standard deviation for the variable. For ions, standard deviation was set as 1/10 x_{ij}, while for PM as 3/10 x_{ij}. This matrix is quite approximate; however it was considered better than no input matrix; otherwise the same standard deviation would be associated to all data matrix. C2 was =0, as usually used[70], while for C3, different values between 0.00 and 0.20 were tested[69,79].

The Robust mode, together with the value of four times the S.D. of the species to define outliers, was used to minimize the distortion of dataset by the outliers[80]. Since there are some ion data below the detection limit (0.5 µg/m^3,as indicated by URG 9000D manual),

the optional parameter "BDLneg r1 r2" was used. As suggested by Paatero[70], r2=10 was used.

The appropriate number of factors extracted and the value of C3 were then determined based on the satisfying of most of the following criteria (the first four criteria were based on Lee et al.[73] and Chan et al.[80]):

- Value of Q close to n x m – p x m – p x n (i.e. the degree of freedom of the analysis).
- R90 (the 90 percentile of the scaled residuals, r_{ij}) is within ±2. That is, most of the residuals are within 2.
- A sharp drop in IM and/or IS
- A significant increase in the largest rotmat element.
- Reasonable estimated source profiles

Two to eight different factors were tested for both the analysis.

For the first one (without PM), only four factors and C3=0.00 were found to obey all the required constraints and resulted in physically meaningful solution. The rotational state of the result has been controlled by the "peaking parameter" FPEAK. Values between -0.5 and 0.5 were tested. With positive FPEAK values, Q values were similar to FPEAK=0, while with negative FPEAK values, changes in Q value were higher. Among positive FPEAK values, the solution with FPEAK=0.1 resulted in the most physically meaningful solution; ROT values were much lower (an order of magnitude) than FPEAK=0 (see Figure 7.2 for IM, IS and ROT values for C3=0.00 and FPEAK=0.1). The optimal Q-value obtained with this model was 3888, which compares reasonably well with the theoretical value of 2259 for the four factor model. The observed difference between theoretical and calculated Q-value (factor of 1.7) is reasonable given the highly empirical nature of the input error values[79]. R90 is within ±2. Specifically, 95% of the residuals are within ±2. Six factors explained >75% of the variations for all species.

For the second PMF analysis (with PM)four factors and C3=0.02 were found to obey all the required constraints and resulted in physically meaningful solution.The fact that both the analysis resolved the same number of factor can be considered as an additional test for

the PMF model. The rotational state of the result has been controlled by the "peaking parameter" FPEAK. Also in this case the solution with FPEAK=0.1 resulted in the most physically meaningful solution, since ROT values were much lower (an order of magnitude) than FPEAK=0 (see Figure 7.3 for IM, IS and ROT values for C3=0.02 and FPEAK=0.1). The optimal Q-value obtained with this model was 4841, which compares reasonably well with the theoretical value of 3624 for the four factor model. The observed difference between theoretical and calculated Q-value (factor of 1.3) is reasonable given the highly empirical nature of the input error values[79].R90 is within ±2. Specifically, 96% of the residuals are within ±2. Six factors explained >75% of the variations for all species.

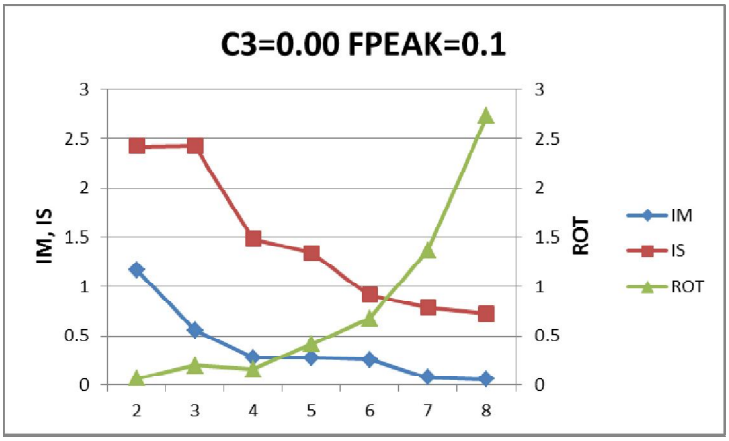

Figure 7.2: Determination of the number of factors, using C1=0.00 and FPEAK=0.1

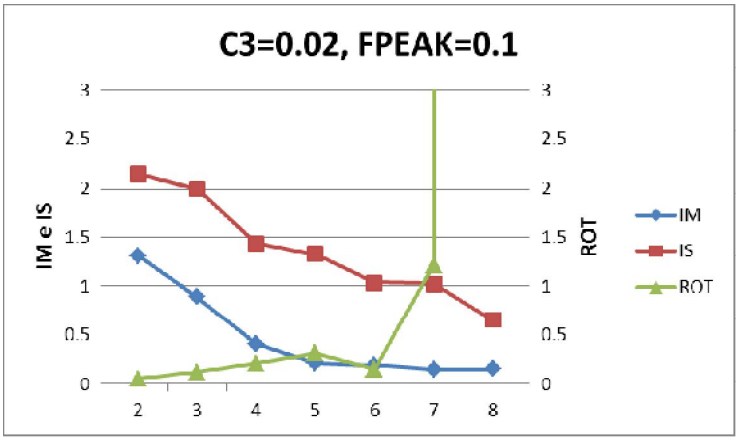

Figure 7.3: Determination of the number of factors, using C1=0.02 and FPEAK=0.1

7.2 RESULTS AND DISCUSSION

7.2.1 Source profile

The source profiles in mass concentration of the four factors are shown in Figure 7.4.

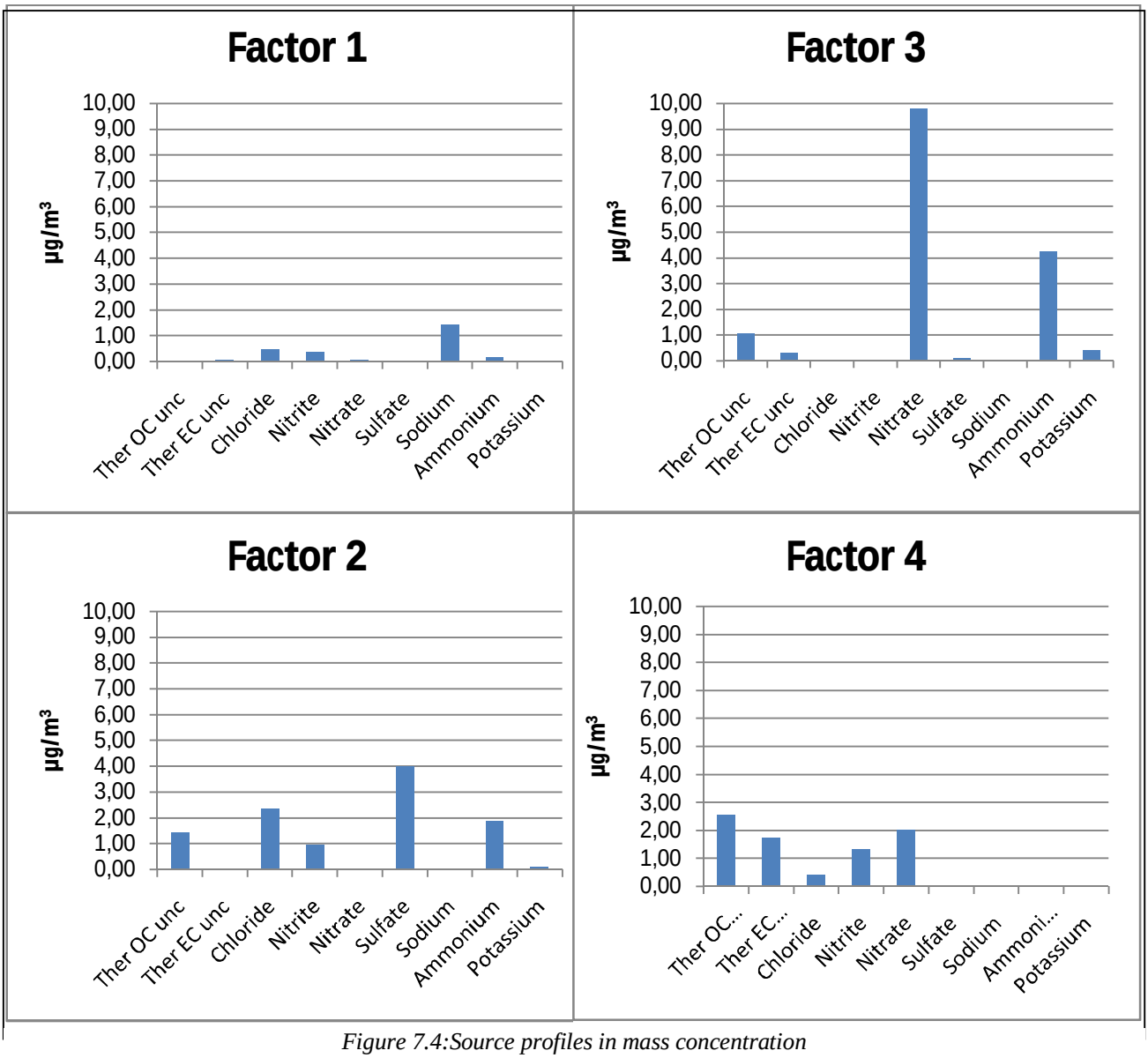

Figure 7.4:Source profiles in mass concentration

The first factor is characterized only by sodium, which is explained only by this factor. Sodium behavior is independent from other variables; the factor is difficult to interpret and it can be also due to some instrumental errors. The second factor is mainly characterized by sulfates, but also from OC, ammonium, chloride and nitrite. It can be identified as secondary ammonium sulfates related to regional transport. Ammonium,

nitrates and potassium are mainly explained by the third factor, which is characterized also by OC and EC. This source can be associated to the conversion of NO_x, which are emitted by both vehicular traffic and other combustion sources. EC is mainly explained by the fourth factor, which can be identified as vehicular traffic contribution.

The last three factors have been identified also in the previous study (chapter 6). Their attribution to the source was deepened in chapter 6.2.2 and further references on their attributions can there be found. Nevertheless some differences can be observed. In this study, in regional transport factor, sulfate is not in excess. It is probably due to the on line analysis of ammonium, which avoids its evaporation during sample analysis. OC concentration in this factor is lower. This can be found in all the factors and it is due to the general lower concentration of OC in this study compared to the one reported in chapter 6. In conversion of NO_xfactor, sulfate contribution is very low. Compared to what is reported in chapter 6, this study is able to completely separate ammonium nitrate from ammonium sulfate.

For secondary ammonium sulfates and conversion of NO_x factors, the characteristic molar ratios were evaluated and they can be considered as an additional analysis for the PMF model. Molar ratio of ammonium to nitrate in conversion of NO_x factor is 1.5, while molar ratio of ammonium to sulfate insecondary ammonium sulfates factor is 1.7. Considering the uncertainty of the PMF model, these results can be considered a good proof of the attribution of these factors to the sources.Moreover they confirm that this study is able to well separate ammonium nitrate from ammonium sulfate.

7.2.2 Factor contribution

G matrix allows to assess how the factors influence the samples. The whole G matrix is reported in Appendix V. From the analysis of the temporal trends of the factors, some considerations appear particularly relevant. Specifically, in Figure 7.5a-b, vehicular traffic factor daily trend is reported, for all the campaign days (a), and the average day (b). The temporal trends confirm the attribution of the factor to the sources. The reported trend is the same as vehicular traffic fluxes: there is a peak at 8:00 a. m., than factor contribution decreases and then it increases again after 5:00 p.m. Usually at night the factor contribution is low. However between the 19th and the 20th of February and the 25th and 26th of February the contribution is particularly high. These are week-end days

(Saturday – Sunday and Friday – Saturday, respectively). Probably during these nights an important event took place in the city and it increased travelling cars.

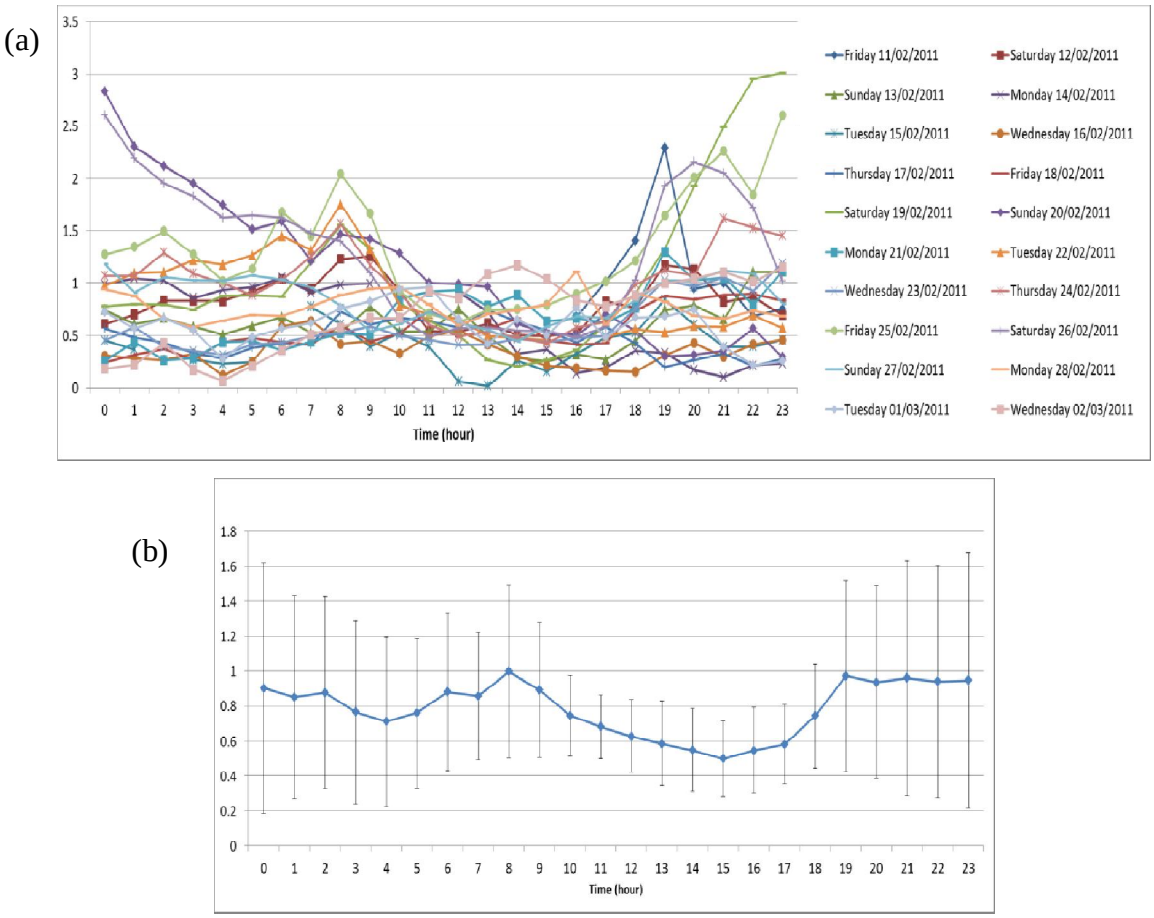

Figure 7.5:Daily trend of vehicular traffic factor (a) for each sampling day and (b) for the average day. Bars represent standard deviation, i.e. data dispersion

Other interesting considerations emerge from the comparison betweenNO_x conversion factor and $PM_{2.5}$ concentration (Figure 7.6). Their trends are very similar; particularly during the days when $PM_{2.5}$ concentration is particularly high (from 13th to 16th February), also the factor contribution strongly increases. This behavior can suggest that $PM_{2.5}$ concentration peaks are especially due to this factor contribution. Therefore, in order to reduce $PM_{2.5}$ air concentration, this source is especially worthy of operating on.

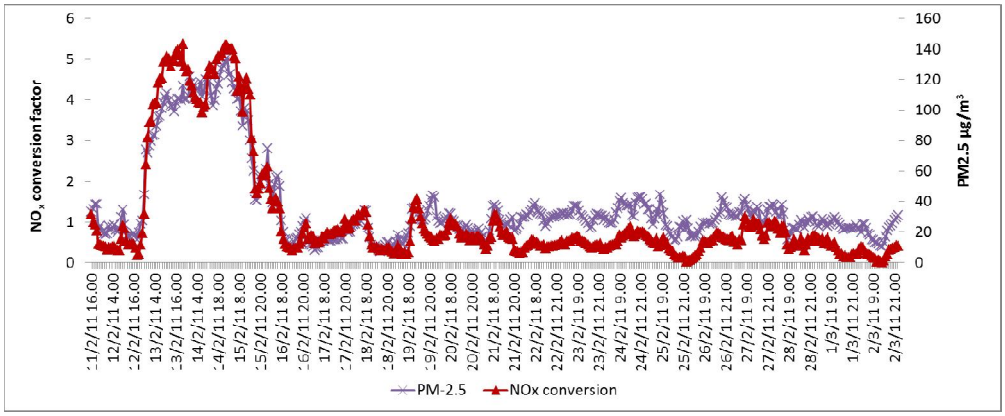

Figure 7.6: Comparison between NO_x conversion factor and $PM_{2.5}$ concentration

The inclusion of the measured particle mass concentrations as independent variables in the PMF modeling allowed to obtain the mass apportionment. The explained variation (EV) values of F matrix are a measure of the contribution of each chemical species in each factor (see chapter 4.2). Therefore they can be useful for an intuitive indication of the significance of a variable in the factor, i.e. how much important is the factor in explaining the variable. This parameter was used to assess the mass apportionment and thus to discriminate which were the main sources of PM. Three PM classes were considered: PM_1, $PM_{2.5-1}$ and $PM_{10-2.5}$. This study is not thus a real mass apportionment, since it was not included only the analyzed PM class (i.e. $PM_{2.5}$). The results should be considered only qualitatively, to assess which sources are responsible of the higher contribution of the above mentioned classes. EV(F) values for PM_1, $PM_{2.5-1}$ and $PM_{10-2.5}$ are reported in Table 7.1. $PM_{10-2.5}$ is almost totally associated with vehicular traffic (72%). This can be mainly due to road dust resuspension. This factor strongly contributes also to $PM_{2.5-1}$, but in this case also NO_x conversion contribution is important (20%). PM_1 behavior is instead different; the main sources are NO_xconversion and regional transport. These sources are both linked to secondary particulate (ammonium nitrate and ammonium sulfate). As expected, secondary particulate dimension is lower than 1 µm, since the fine mode has a peak between 0.15 and 0.5[14].

Table 7.1: EV(F) values for PM_1, $PM_{2.5-1}$ and $PM_{10-2.5}$.

	PM(10÷2.5)	**PM(2.5÷1)**	**PM1**
Sodium	0.00	0.03	0.00
Vehiculartraffic	0.72	0.53	0.12
NO_xconversion	0.00	0.20	0.44
Regionaltransport	0.06	0.00	0.32
Residuals	0.22	0.24	0.11

7.3 CONCLUSION

PMF analysis proved to be a valid support in atmospheric pollution studies. The analysis identified four factors; three of them can be associated with specific sources of the determined compounds: vehicular traffic, NO_x conversion and regional transport. The fourth factor is instead probably due to an independent behavior of sodium.

This PMF analysis was able to completely separate ammonium nitrate from ammonium sulfate and the obtained molar ratios values confirm this consideration

The peaks in $PM_{2.5}$ concentrations seem especially due to the contribution of NO_x conversion source. Therefore, in order to reduce $PM_{2.5}$ air concentration, this source is especially worthy of operating on.

Vehicular traffic is the main source of $PM_{10-2.5}$ and $PM_{2.5-1}$ fractions (they are probably due to soil dust resuspension), while PM_1 origin is mainly secondary.

8 Final remarks

How to effectively mitigate the pollutantemissions in atmosphere is an international and imperative issue. Nowadays one of the main topic for scientific researchers is assessing the contribution that each emission source makes on the environment, in order to set the sources it is necessary to operate on the most to reduce air pollution. The source apportionment techniques are now well established to develop this information for informed decision making. Nevertheless the development and the application of innovative source apportionment methodsare fundamental in order to go deeper in identifying the contribution of different emission sources to the total pollutant amount.

In this work, two main research lines have been followed in order to go deeper in source apportionment studies.

For what concerns the first line, the potentiality of the use of PM samplers coupled with a wind select sensor, in order to sample only the air masses influenced by specific emission sources, has been assessed, since it is still little used. Moreover, new specific markers have been investigated in order to obtain more complete and quantitative information on the sources affecting the area, particularly focusing on the processes of biomass burning.

The second research line consists in the application of new statistical tools in data analysis.Positive Matrix factorization (PMF) is a new approach compared to Principal Component Analysis (PCA); it is more powerful and provides quantitative information on source contributions.This new technique has been applied to datasets which refer to different time resolution data.

The project is developed mainly by the study of atmospheric emission sources in a suburban area influenced by a municipal solid waste incinerator (MSWI), a medium-sized coastal tourist town and a motorway.

The main results were:

- The sampling technique based on two PM samplers coupled with a wind select sensor may be a valid support in source apportionment studies. However, meteorological and territorial conditions could strongly affect the results. The

technique is suitable for areas characterized by moderate winds and with few prevailing directions, as in the case of costal zones.

- Apart from well-known combustion marker determination, new outdoor biomass burning indicators were found. Ammonium and nitrates were found in the coarse and in the PM10-TSP fractions, unlike what is reported in the literature and what is found in the other samples of the campaign. Lead and aluminium in $PM_{2.5}$ can be considered representative biomass combustion indicators. Surprisingly, even if potassium concentration is higher during bonfire event, PM is not enriched of this well-known combustion marker
- The application of PMF analysis to $PM_{2.5}$ collected with samplers coupled with a wind select sensor allows to obtain more detailed results on the sources affecting the area compared to a classical PMF analysis. This is mainly due to the higher environmental information that samples collected with this new sampling technique have. PMF was also applied to datasets which refer to different time resolution data in order to have a complete overview of the potential of the technique. Results demonstrated that the higher the temporal resolution of the data is, the more the source profiles are close to the real one and mixed profiles, which represent more than one source, are not present.

8.1 PUBLICATIONS

The research studies showed in this thesis are also illustrated in scientific papers that are at the moment submitted to scientific journals with impact factor.

Specifically, three papers are submitted:

- "Source apportionment study based on selective wind direction sampling" is submitted to "Environmental Monitoring and Assessment"
- "Bulk deposition close to a Municipal Solid Waste incinerator: one source among many" is submitted to "The Science of the Total Environment". Major revision was suggested for the paper and at the moment the revised manuscript has been submitted.
- "New environmental indicators for open bonfire: a case study" is submitted to "Atmospheric Environment"

The research studies showed in this thesis were already presented to several congresses and conferences. Specifically, the following studies have been presented:

- Meeting “PM2010” (Venice (I), 18th-20th May 2010): poster presentation “Discrimination ofcontamination sources in an area near a MSW incinerator based on selective wind direction sampling”
- “XII National Meeting of Environmental and Cultural Heritage Chemistry” (Taormina (I), 26th -30thSeptember 2010): poster presentation “Directional PM10 sampling: determination of PAHs and Pd toassess vehicular traffic contribution”
- 14a Fair “Ecomondo" (Rimini (I), 3rd-6th November 2010), Conference "Industrial emission sourcesof organic and inorganic micropollutants: energy production, metallurgic industry and wastemanagement": platform presentation “Directional PM10sampling: determination of PAHs to assess sources contribution”
- Meeting “SETAC Europe 2011” (Milan (I), 15th-19th May 2011): platform presentation “Atmosphericdeposition fluxes of contaminants close to a municipal solid waste incinerator”
- “XIV National Meeting of Chemical Italian Society” (Lecce (I), 11th -16th September 2011): coauthorof the platform presentation “Atmospheric pollutant deposition flow close to a municipal solid wasteincinerator: 5 years-monitoring results”
- “XI Chemistry day of Emilia-Romagna region” (Modena (I), 28th October 2011): poster presentation“Biomass burning influence on chemical composition of particulate matter”
- 15a Fair “Ecomondo" (Rimini (I), 9th-12th November 2011), Conference "Energy and Environmentregional platform: industrial research at Technopoles and companies working in this field ": platformpresentation “Directional PM10 sampling: determination of PAHs to assess sources contribution”
- Meeting “PM2012” (Perugia (I), 16th-18th May 2012): platform presentation “PMF analysis applied toatmospheric deposition fluxes in an area close to a MSW incinerator”
- “XXIII National Meeting of Analytical Chemistry” (Elba Island (I), 16th -20th September 2012): poster presentation “Source apportionment study near a MSW incinerator by Positive Matrix Factorization (PMF)”

- 16a Fair “Ecomondo" (Rimini (I), 7th-10th November 2012), Conference "Atmospheric pollution:environmental monitoring experiences in Italian case study ": poster presentation “PMF analysisapplied to bulk atmospheric deposition near a Municipal Solid Waste incinerator”
- Training seminary "Atmospheric pollution study: high time resolution chemical-physicalcharacterization of atmospheric pollutants" (Bologna (I), 28th November 2012): platform presentation:" Source apportionment analysis of urban site online data by PMF analysis"

9 Appendices

APPENDIX I: DATA ON WIND SPEED, WIND DIRECTION AND RAINFALL FOR EACH SAMPLING MONTH

		Mean wind speed (m/s)	Median wind speed (m/s)	Max wind speed (m/s)	Prevalentwinddirection	Rainfall (mm)
2006	17/01/06-14/02/06	2.5	1.8	12.8	ONO	8.68
	15/02/06-17/03/06	3.8	3.1	20.1	SO	69.87
	18/03/06-21/04/06	2.9	2.4	12.2	OSO	71.99
	22/04/06-12/05/06	2.4	2.1	10.9	OSO	30.70
	13/05/06-26/05/06	2.7	2.2	11.2	OSO	11.45
	27/05/06-19/06/06	2.7	2.4	9.5	OSO	63.09
	20/06/06-25/07/06	2.3	2.1	6.5	OSO	22.36
	26/07/06-07/09/06	2.4	2.0	9.9	OSO	119.33
	08/09/06-06/10/06	2.6	2.3	11.0	OSO	125.26
	07/10/06-16/11/06	2.1	1.7	8.5	OSO	17.27
	17/11/06-20/12/06	2.5	1.9	10.3	O	38.13
	21/12/06-22/01/07	2.4	1.6	14.3	OSO	13.33
2007	23/01/07-01/03/07	2.9	2.3	9.7	OSO	29.10
	02/03/07-02/04/07	3.3	2.6	16.3	OSO	124.70
	03/04/07-08/05/07	2.2	2.0	9.9	OSO	37.25
	09/05/07-08/06/07	2.9	2.7	10.9	OSO	29.20
	09/06/07-10/07/07	3.5	3.1	16.3	OSO	8.69
	11/07/07-09/08/07	3.0	2.6	12.3	OSO	20.46
	10/08/07-10/09/07	2.6	2.2	8.2	OSO	107.71
	11/09/07-19/10/07	2.6	2.3	12.3	OSO	44.17
	20/10/07-30/11/07	3.1	2.4	11.9	O	74.74
	1/12/07-19/02/08	2.8	2.2	12.2	O	63.27
2008	20/02/08-24/03/08	3.6	2.6	16.9	OSO	112.98
	25/03/08-04/05/08	3.1	2.5	15.3	OSO	69.63
	05/05/08-04/06/08	2.5	2.2	9.8	OSO	47.71
	05/06/08-14/07/08	2.7	2.2	9.9	OSO	12.75
	15/07/08-05/09/08	2.8	2.3	12.8	OSO	42.08
	06/09/08-24/10/08	2.6	2.1	9.6	OSO	53.26
	25/10/08-19/12/08	3.1	2.3	14.8	O	161.08
	20/12/08-23/01/09	2.9	2.3	14.7	O	54.10
2009	24/01/09-12/03/09	3.0	2.5	13.1	O	171.36
	13/03/09-17/04/09	3.5	2.6	15.0	OSO	44.92
	18/04/09-21/05/09	2.6	2.3	8.8	ONO	27.67
	22/05/09-22/06/09	3.0	2.6	10.7	ONO	64.38
	23/06/09-24/07/09	2.7	2.2	10.3	O	26.20
	25/07/09-24/08/09	2.5	2.0	7.4	ENE	2.40
	25/08/09-1/10/09	2.7	2.5	9.4	ONO	33.71
	2/10/09-2/11/09	2.8	2.3	11.7	O	139.31
	3/11/09-11/12/09	2.7	2.0	12.1	ONO	56.72
	12/12/09-15/01/10	3.3	2.5	13.4	O	166.67
2010	16/01/10-16/02/10	3	2.3	12.4	O	116.23
	17/02/10-15/03/10	3.2	2.5	12.4	ENE	137.62
	16/03/10-22/04/10	2.7	2.2	15.3	ONO	82.95
	23/04/10-25/05/10	2.6	2.3	9.0	ONO	136.17
	26/05/10-28/06/10	2.5	2.2	9.6	ONO	96.69
	29/06/10-03/08/10	2.4	2.1	8.2	OSO	32.26
	04/08/10-01/09/10	2.5	2.1	9.2	OSO	49.91
	02/09/10-08/10/10	2.8	2.4	11.7	OSO	128.41
	09/10/10-08/11/10	3.0	2.5	8.2	O	82.86
	09/11/10-06/12/10	2.8	2.2	14.2	OSO	148.46
	07/12/10-17/01/11	2.4	1.9	10.6	ONO	50.63

APPENDIX II: DEPOSITION FLUXES (MG/M2DAY) OF SOLUBLE IONS.

		Nitrates				Sulfates			
		mg/m^{2}d							
		Site 1	Site 2	Site 3	Site 4	Site 1	Site 2	Site 3	Site 4
2006	17/01/06-14/02/06	16	7.8	15	5.1	14	15	32	10
	15/02/06-17/03/06	6.7	8.9	8.1	6.8	7.7	11	10	8.6
	18/03/06-21/04/06	9.3	9.6	12	16	7.3	7.1	7.5	7.2
	22/04/06-12/05/06	28	15	13	13	3.7	4.2	5.0	4.6
	13/05/06-26/05/06	17	22	7.2	18	4.5	4.7	5.0	4.7
	27/05/06-19/06/06	9.1	7.2	9.7	8.5	4.2	3.0	4.1	5.1
	20/06/06-25/07/06	4.8	5.3	4.8	5.1	3.0	2.8	2.8	3.8
	26/07/06-07/09/06	6.6	12	16	6.5	4.7	4.3	4.7	4.8
	08/09/06-06/10/06	8.6	1.0	8.7	1.3	5.5	6.2	4.8	4.6
	07/10/06-16/11/06	3.8	1.1	5.5	0.033	2.0	3.0	2.9	1.9
	17/11/06-20/12/06	5.1	5.6	6.7	4.1	5.0	5.2	6.1	4.7
	21/12/06-22/01/07	4.0	3.8	4.7	3.3	4.5	4.3	6.3	3.7
2007	23/01/07-01/03/07	4.8	4.5	4.9	4.3	2.4	2.1	2.5	2.5
	02/03/07-02/04/07	22	17	27	17	21	16	23	19
	03/04/07-08/05/07	5.1	4.9	4.5	3.6	2.6	3.4	3.8	2.4
	09/05/07-08/06/07	4.2	4.6	5.2	3.7	2.7	3.4	3.3	3.4
	09/06/07-10/07/07	2.1	3.2	2.8	1.9	1.6	1.5	1.5	1.6
	11/07/07-09/08/07	7.2	8.1	8.9	7.0	4.9	5.1	5.6	5.2
	10/08/07-10/09/07	10	10	11	9.9	0.10	0.080	0.060	0.10
	11/09/07-19/10/07	8.3	7.4		1.7	6.3	5.5		1.6
	20/10/07-30/11/07	6.8	6.9		4.9	9.9	10		5.2
	1/12/07-19/02/08	4.2	3.5	4.6	3.5	3.7	3.9	3.9	8.2
2008	20/02/08-24/03/08	8.9	8.4	10	8.3	16	15	17	16
	25/03/08-04/05/08	7.8	7.2	8.0	6.8	4.0	4.0	4.2	3.9
	05/05/08-04/06/08	4.6	4.4	4.8	2.9	4.9	5.6	5.3	3.7
	05/06/08-14/07/08	0.32	0.095	1.7	0.73	0.18	0.059	1.0	5.2
	15/07/08-05/09/08	11	4.0	4.0	0.26	4.2	3.3	3.1	2.7
	06/09/08-24/10/08	1.8	2.1	6.4	3.5	5.1	5.1	4.9	4.2
	25/10/08-19/12/08	53	4.8	6.1	6.2	4.8	4.2	4.7	4.6
	20/12/08-23/01/09	4.6	6.6	6.1	5.8	7.9	10	11	12
2009	24/01/09-12/03/09	7.2		7.5	9.3	8.0		9.9	8.9
	13/03/09-17/04/09	5.3	5.7	4.9	5.3	5.5	5.1	4.1	4.5
	18/04/09-21/05/09	5.5	4.9	5.8	3.0	5.5	4.4	5.8	5.4
	22/05/09-22/06/09	6.0	4.4	6.4	5.5	6.0	6.5	6.8	5.8
	23/06/09-24/07/09	5.4	3.8	4.6	0.042	2.7	2.4	2.7	2.5
	25/07/09-24/08/09	1.2	3.4	1.1	0.64	1.3	1.1	1.7	1.2
	25/08/09-1/10/09	4.8	4.1	4.6	4.4	3.6	5.6	6.1	3.9
	2/10/09-2/11/09	8.4	10	9.1	10	5.7	5.8	6.9	7.0
	3/11/09-11/12/09	5.1	4.8	5.5	5.1	2.9	2.8	3.0	3.4
	12/12/09-15/01/10	6.9	6.5	6.9	9.5	4.4	4.1	4.6	5.4
2010	16/01/10-16/02/10	8.3	11	9.4	11	9.9	15	11	14
	17/02/10-15/03/10	9.7	8.7	8.7	11	20	17	18	25
	16/03/10-22/04/10	4.3	4.2	4.7	4.7	2.9	3.0	3.2	3.7
	23/04/10-25/05/10	5.5	5.3	5.6	3.4	8.5	7.8	8.0	8.2
	26/05/10-28/06/10	4.3	6.1	5.8	4.5	4.4	4.7	4.1	4.1
	29/06/10-03/08/10	3.3	4.9	5.3	1.7	1.9	2.2	2.6	2.7
	04/08/10-01/09/10	4.9	4.1	4.5	3.9	3.0	3.1	2.7	2.1
	02/09/10-08/10/10	4.7	6.5	5.9		5.4	3.5	4.6	
	09/10/10-08/11/10	5.4	4.2	5.8		6.6	6.6	7.6	
	09/11/10-06/12/10	4.3	3.7	4.4		1.7	1.6	1.9	
	07/12/10-17/01/11	5.1	5.4	5.0		2.6	2.6	2.9	

		Chlorides				**Fluorides**			
		mg/m^{2}d							
		Site 1	Site 2	Site 3	Site 4	Site 1	Site 2	Site 3	Site 4
2006	17/01/06-14/02/06	56	62	150	39	0.080	0.026	0.12	0.068
	15/02/06-17/03/06	24	48	43	27	0.047	0.057	0.049	0.016
	18/03/06-21/04/06	9.8	11	11	10	0.044	0.046	0.046	0.058
	22/04/06-12/05/06	5.6	4.8	8.7	5.4	0.028	0.030	0.040	0.048
	13/05/06-26/05/06	2.8	1.9	2.5	1.5	0.044	0.052	0.035	0.064
	27/05/06-19/06/06	20	14	19	21	0.042	0.042	0.040	0.043
	20/06/06-25/07/06	1.8	1.7	2.7	1.4	0.028	0.027	0.028	0.036
	26/07/06-07/09/06	9.2	8.8	9.2	8.6	0.018	0.062	0.070	0.021
	08/09/06-06/10/06	10	11	12	11	0.054	0.052	0.022	0.031
	07/10/06-16/11/06	4.2	5.2	7.4	4.2	0.020	0.024	0.030	0.029
	17/11/06-20/12/06	14	17	18	13	0.039	0.041	0.045	0.033
	21/12/06-22/01/07	12	14	24	14	0.032	0.022	0.031	0.020
2007	23/01/07-01/03/07	2.5	1.4	2.8	1.9	0.023	0.020	0.022	0.022
	02/03/07-02/04/07	60	51	69	51	0.19	0.15	0.18	0.14
	03/04/07-08/05/07	4.0	4.9	5.5	3.7	0.032	0.036	0.035	0.038
	09/05/07-08/06/07	2.6	2.1	3.0	1.4	0.027	0.035	0.031	0.030
	09/06/07-10/07/07	2.2	2.2	2.3	1.7	0.016	0.014	0.016	0.020
	11/07/07-09/08/07	6.7	11	13	8.7	0.038	0.036	0.035	0.14
	10/08/07-10/09/07	30	27	23	33	0.053	0.038	0.062	**0.010**
	11/09/07-19/10/07	12	11		3.8	0.050	0.040		0.020
	20/10/07-30/11/07	33	35		23	0.10	0.080		0.060
	1/12/07-19/02/08	10	12	11	10	0.030	0.025	0.036	0.043
2008	20/02/08-24/03/08	60	59	66	62	0.070	0.065	0.080	0.074
	25/03/08-04/05/08	6.4	6.4	7.0	6.7	0.043	0.051	0.041	0.057
	05/05/08-04/06/08	4.9	5.2	4.8	3.4	0.078	0.057	0.057	0.67
	05/06/08-14/07/08	0.49	0.44	0.95	2.4	0.0029	**0.00015**	0.013	0.031
	15/07/08-05/09/08	4.5	3.7	4.4	3.6	0.035	0.047	0.048	0.057
	06/09/08-24/10/08	7.0	6.7	11	5.7	0.043	0.030	0.073	0.025
	25/10/08-19/12/08	8.3	7.4	8.7	7.7	0.040	**0.0050**	0.030	0.040
	20/12/08-23/01/09	25	31	35	39	0.020	0.030	**0.0050**	**0.0050**
2009	24/01/09-12/03/09	14		17	17	0.040		0.040	0.044
	13/03/09-17/04/09	20	14	11	8.9	0.025	0.024	0.028	0.020
	18/04/09-21/05/09	4.3	4.0	5.0	3.0	0.028	0.026	0.030	0.027
	22/05/09-22/06/09	15	14	20	15	0.024	0.021	0.020	0.028
	23/06/09-24/07/09	2.4	2.3	3.7	3.0	0.016	0.011	0.015	0.022
	25/07/09-24/08/09	1.2	1.1	1.5	1.5	0.0071	0.0053	0.0069	0.014
	25/08/09-1/10/09	9.4	15	19	8.6	0.015	0.017	0.019	0.019
	2/10/09-2/11/09	18	19	24	24	0.032	0.027	0.019	0.033
	3/11/09-11/12/09	5.7	5.2	7.1	7.3	0.020	0.019	0.022	0.029
	12/12/09-15/01/10	8.1	7.4	9.4	10	0.020	0.022	0.025	0.13
2010	16/01/10-16/02/10	15	19	19	21	0.036	**0.020**	0.047	0.056
	17/02/10-15/03/10	50	42	50	56	0.051	**0.034**	0.042	0.081
	16/03/10-22/04/10	3.9	4.2	5.1	5.2	0.017	0.032	0.022	0.034
	23/04/10-25/05/10	8.5	6.7	9.3	9.0	0.046	**0.036**	0.039	0.052
	26/05/10-28/06/10	6.1	6.7	6.0	6.7	0.024	0.026	0.028	0.036
	29/06/10-03/08/10	3.0	2.4	4.3	3.2	0.017	0.017	0.019	0.035
	04/08/10-01/09/10	5.4	7.1	5.4	3.1	0.016	0.020	0.016	0.017
	02/09/10-08/10/10	5.1	8.8	14		0.034	0.028	0.030	
	09/10/10-08/11/10	11	12	15		0.029	0.034	0.037	
	09/11/10-06/12/10	2.8	2.4	3.2		0.026	0.22	**0.026**	
	07/12/10-17/01/11	6.8	6.6	8.4		0.020	0.010	0.020	

		Nitrites				**Sodium**			
		mg/m^{2}d							
		Site 1	Site 2	Site 3	Site 4	Site 1	Site 2	Site 3	Site 4
2006	17/01/06-14/02/06	0.22	0.18	0.42	0.10	35	26	83	24
	15/02/06-17/03/06	**0.020**	0.12	0.12	0.025	13	16	23	15
	18/03/06-21/04/06	0.28	0.074	0.14	0.27	4.6	5.7	5.3	4.8
	22/04/06-12/05/06	0.054	0.33	**0.020**	**0.015**	2.0	2.0	4.0	2.4
	13/05/06-26/05/06	0.10	0.11	0.12	0.10	1.4	1.3	1.3	1.1
	27/05/06-19/06/06	0.77	0.44	0.58	0.65	9.8	7.1	9.3	10
	20/06/06-25/07/06	0.18	0.078	0.15	0.056	0.62	0.60	1.0	0.59
	26/07/06-07/09/06	**0.030**	**0.030**	0.28	**0.030**	0.71	0.67	1.0	0.88
	08/09/06-06/10/06	**0.040**	3.2	**0.045**	**0.045**	0.47	0.47	0.91	0.62
	07/10/06-16/11/06	1.9	7.5	0.42	0.014	0.58	0.75	1.1	0.63
	17/11/06-20/12/06	0.29	**0.015**	0.30	**0.010**	2.1	2.4	2.8	1.9
	21/12/06-22/01/07	0.63	0.66	0.71	0.48	1.7	2.0	3.3	2.0
2007	23/01/07-01/03/07	0.24	0.24	0.23	0.20	0.32	0.21	0.42	0.29
	02/03/07-02/04/07	**0.045**	**0.040**	**0.040**	**0.045**	8.9	7.3	10	7.6
	03/04/07-08/05/07	**0.010**	0.12	0.39	**0.010**	0.61	0.73	0.88	0.55
	09/05/07-08/06/07	0.11	0.25	0.22	0.12	0.35	0.42	0.49	0.32
	09/06/07-10/07/07	0.053	0.083	**0.0050**	0.062	0.34	0.36	0.42	0.25
	11/07/07-09/08/07	0.12	0.13	0.12	0.12	3.7	5.2	6.2	4.4
	10/08/07-10/09/07	0.24	0.13	0.43	0.17	5.2	4.4	5.1	5.7
	11/09/07-19/10/07	0.18	0.26		**0.015**	1.8	1.6		1.0
	20/10/07-30/11/07	0.23	0.19		0.14	5.0	5.5		3.5
	1/12/07-19/02/08	**0.010**	0.17	0.21	0.19	1.6	0.35	0.30	0.19
2008	20/02/08-24/03/08	0.15	0.14	0.082	0.16	11	10	11	11
	25/03/08-04/05/08	0.11	0.12	0.16	0.13	0.75	0.76	0.90	0.82
	05/05/08-04/06/08	0.090	0.13	0.10	0.082	0.40	0.44	0.44	0.16
	05/06/08-14/07/08	0.014	**0.00050**	0.018	**0.010**	0.071	0.064	0.32	0.81
	15/07/08-05/09/08	**0.010**	0.23	0.36	**0.010**	1.5	2.8	3.1	1.0
	06/09/08-24/10/08	0.54	0.86	0.17	0.086	4.8	5.1	7.2	4.1
	25/10/08-19/12/08	0.28	0.19	0.19	**0.035**	6.0	5.4	6.4	6.6
	20/12/08-23/01/09	0.12	0.14	**0.015**	**0.020**	17	19	23	25
2009	24/01/09-12/03/09	0.29		0.32	0.31	11		9.4	18
	13/03/09-17/04/09	0.13	0.17	0.091	**0.027**	12	9.1	7.2	6.3
	18/04/09-21/05/09	0.14	0.17	0.18	0.033	2.5	2.3	3.0	2.2
	22/05/09-22/06/09	0.52	**0.037**	1.3	2.4	12	9.2	15	11
	23/06/09-24/07/09	0.090	0.074	0.014	0.055	1.7	1.6	2.3	2.3
	25/07/09-24/08/09	0.13	**0.0049**	**0.0049**	0.042	0.78	0.92	1.0	0.74
	25/08/09-1/10/09	0.22	2.1	0.41	0.071	6.5	9.6	12	5.8
	2/10/09-2/11/09	0.12	0.090	0.11	0.14	12	13	16	17
	3/11/09-11/12/09	0.028	0.13	0.16	0.11	3.6	3.3	3.8	4.3
	12/12/09-15/01/10	0.16	0.14	0.14	0.17	5.6	5.1	6.5	7.1
2010	16/01/10-16/02/10	0.087	0.082	0.10	0.066	8.5	11	11	12
	17/02/10-15/03/10	0.14	0.12	0.11	0.12	26	23	26	31
	16/03/10-22/04/10	0.087	0.058	0.14	0.081	2.2	2.3	2.6	2.6
	23/04/10-25/05/10	0.15	0.14	0.065	0.077	4.3	3.5	4.8	4.6
	26/05/10-28/06/10	0.13	0.50	0.34	0.15	3.9	4.2	3.6	3.9
	29/06/10-03/08/10	0.22	0.13	0.15	0.037	1.8	1.7	2.7	1.6
	04/08/10-01/09/10	0.11	0.076	0.10	0.089	3.4	4.5	3.4	2.0
	02/09/10-08/10/10	0.17	0.19	0.075		3.3	2.7	3.7	
	09/10/10-08/11/10	0.17	0.11	0.16		7.1	7.8	8.8	
	09/11/10-06/12/10	0.25	0.18	0.28		1.0	1.3	1.8	
	07/12/10-17/01/11	0.43	0.37	0.51		3.5	3.5	4.2	

		Potassium				**Ammonium**			
		mg/m^{2}d							
		Site 1	Site 2	Site 3	Site 4	Site 1	Site 2	Site 3	Site 4
2006	17/01/06-14/02/06	2.5	1.6	3.9	1.2	**0.0050**	**0.0050**	**0.0050**	**0.0050**
	15/02/06-17/03/06	1.2	1.3	1.5	0.85	1.4	2.1	0.20	1.7
	18/03/06-21/04/06	0.97	1.0	0.78	2.6	5.5	5.3	4.1	3.6
	22/04/06-12/05/06	0.73	0.68	0.013	0.011	3.3	2.9	1.7	1.0
	13/05/06-26/05/06	1.2	0.87	0.87	0.52	2.3	2.6	1.8	1.3
	27/05/06-19/06/06	0.68	0.69	0.68	1.2	2.3	2.0	1.4	1.6
	20/06/06-25/07/06	0.49	0.31	0.42	0.42	0.21	0.16	0.44	1.1
	26/07/06-07/09/06	1.2	0.58	0.46	0.61	4.2	3.9	3.3	3.3
	08/09/06-06/10/06	0.94	0.76	0.58	0.31	4.7	7.9	3.8	1.6
	07/10/06-16/11/06	0.34	1.1	0.37	0.24	0.49	1.2	1.2	**0.010**
	17/11/06-20/12/06	0.92	0.46	1.1	0.38	1.4	1.5	1.8	0.93
	21/12/06-22/01/07	0.13	0.078	0.18	0.13	1.9	1.9	2.4	1.2
2007	23/01/07-01/03/07	0.29	0.060	0.070	0.063	1.0	0.45	1.2	1.0
	02/03/07-02/04/07	7.3	4.0	10	5.3	4.8	4.7	6.9	3.8
	03/04/07-08/05/07	0.47	0.90	0.95	0.74	**0.020**	1.3	1.0	**0.030**
	09/05/07-08/06/07	0.33	3.6	3.0	2.8	**0.020**	0.41	**0.020**	**0.025**
	09/06/07-10/07/07	0.26	0.28	0.29	0.39	**0.11**	**0.0050**	**0.010**	7.1
	11/07/07-09/08/07	0.25	0.63	0.62	0.65				
	10/08/07-10/09/07	0.55	0.52	0.64	0.32	**0.10**	**0.80**	**0.60**	**0.10**
	11/09/07-19/10/07	0.24	0.49		0.080	1.8	1.9		0.34
	20/10/07-30/11/07	0.59	0.76		0.73	1.8	1.8		0.62
	1/12/07-19/02/08	0.19	0.21	0.21	0.13	7.5	10	8.7	5.6
2008	20/02/08-24/03/08	1.2	0.64	1.0	1.6	**0.080**	**0.075**	**0.080**	**0.090**
	25/03/08-04/05/08	0.53	0.23	0.23	0.23	2.0	2.3	2.1	0.77
	05/05/08-04/06/08	0.80	0.92	0.63	0.022	0.72	2.5	0.87	**0.030**
	05/06/08-14/07/08	0.18	0.34	0.43	1.2	**0.0025**	**0.0016**	**0.0050**	**0.020**
	15/07/08-05/09/08	7.2	3.3	2.2	1.4	1.6	2.6	1.3	0.65
	06/09/08-24/10/08	8.1	4.9	3.9	2.7	9.0	4.0	3.6	1.5
	25/10/08-19/12/08	0.74	3.0	**0.010**	**0.010**	1.8	1.9	1.8	0.80
	20/12/08-23/01/09	2.1	1.7	2.6	2.8	1.9	3.6	3.4	2.5
2009	24/01/09-12/03/09	**0.012**		0.73	0.62	1.4		1.8	2.3
	13/03/09-17/04/09	0.66	0.58	0.54	0.28	2.0	1.0	0.62	0.67
	18/04/09-21/05/09	0.63	0.39	0.54	0.53	1.6	1.6	2.1	0.48
	22/05/09-22/06/09	0.73	1.8	0.55	0.46	2.1	5.0	1.6	**0.12**
	23/06/09-24/07/09	0.17	0.31	0.34	0.33	0.71	0.49	0.63	**0.045**
	25/07/09-24/08/09	0.62	0.18	0.67	0.51	0.069	**0.012**	0.063	**0.025**
	25/08/09-1/10/09	0.40	0.60	0.51	0.0048	1.0	3.3	2.7	**0.034**
	2/10/09-2/11/09	0.95	4.0	0.60	0.80	1.8	1.9	1.5	1.3
	3/11/09-11/12/09	0.59	0.35	1.7	1.2	1.6	2.1	1.3	0.68
	12/12/09-15/01/10	0.030	0.69	0.030	0.27	1.3	1.7	1.5	1.5
2010	16/01/10-16/02/10	0.36	1.8	0.14	0.34	2.0	3.4	2.3	2.3
	17/02/10-15/03/10	**0.032**	0.66	1.4	0.53	2.5	2.6	2.0	2.7
	16/03/10-22/04/10	0.52	0.51	0.42	0.52	1.7	2.1	1.5	0.68
	23/04/10-25/05/10	0.73	0.56	0.63	0.46	3.0	2.3	1.9	0.42
	26/05/10-28/06/10	0.90	0.71	0.78	0.35	3.5	2.9	1.1	0.84
	29/06/10-03/08/10	0.68	0.39	0.54	0.68	1.0	0.84	1.1	0.17
	04/08/10-01/09/10	0.66	0.62	0.24	0.44	2.2	2.2	1.1	0.14
	02/09/10-08/10/10	0.99	0.52	0.74		8.8	2.8	4.4	
	09/10/10-08/11/10	0.44	0.64	1.2		2.2	3.5	2.1	
	09/11/10-06/12/10	0.45	0.39	**0.036**		0.76	1.4	1.2	
	07/12/10-17/01/11	0.18	0.010	0.31		1.2	1.2	1.3	

		Calcium				**Magnesium**			
		mg/m^{2}d							
		Site 1	Site 2	Site 3	Site 4	Site 1	Site 2	Site 3	Site 4
2006	17/01/06-14/02/06	13	8.8	19	9.0				
	15/02/06-17/03/06	6.6	5.6	6.0	5.4				
	18/03/06-21/04/06	6.0	6.5	6.4	7.6				
	22/04/06-12/05/06	6.0	5.4	4.2	5.4				
	13/05/06-26/05/06	9.4	8.3	8.2	8.8				
	27/05/06-19/06/06	4.4	4.2	5.5	5.9				
	20/06/06-25/07/06	5.5	5.0	5.2	6.1				
	26/07/06-07/09/06	5.1	4.4	5.8	5.2	0.51	0.27	0.47	0.34
	08/09/06-06/10/06	2.8	3.0	3.0	3.5	0.19	0.49	0.46	0.27
	07/10/06-16/11/06	2.7	3.2	3.1	4.3	0.14	0.30	0.39	0.090
	17/11/06-20/12/06	8.0	3.6	3.6	3.5	0.52	0.88	1.2	0.88
	21/12/06-22/01/07	1.6	0.70	1.6	1.1	0.31	0.25	0.59	0.36
2007	23/01/07-01/03/07	4.5	2.4	3.4	3.3	0.13	0.10	0.12	0.15
	02/03/07-02/04/07	120	53	72	81	16	11	16	15
	03/04/07-08/05/07	2.8	3.5	2.9	5.7	0.45	0.55	0.62	0.49
	09/05/07-08/06/07	4.2	4.9	4.0	4.3	0.36	0.51	0.46	0.36
	09/06/07-10/07/07	2.3	2.2	1.9	2.5	0.25	0.25	0.26	0.21
	11/07/07-09/08/07	6.3	7.0	6.3	8.1	0.65	1.0	1.1	0.85
	10/08/07-10/09/07	6.4	6.3	6.3	12	2.6	2.4	2.0	2.7
	11/09/07-19/10/07	5.8	5.0		3.3	0.86	0.99		0.64
	20/10/07-30/11/07	5.4	3.1		12	2.9	2.8		2.4
	1/12/07-19/02/08	1.4	1.5	1.6	1.6	0.69	0.72	0.69	0.69
2008	20/02/08-24/03/08	7.3	13	10	10	3.9	4.2	3.7	4.4
	25/03/08-04/05/08	6.5	6.6	11	8.4	0.36	0.30	0.86	0.51
	05/05/08-04/06/08	10	11	11	13	0.51	0.48	0.59	0.19
	05/06/08-14/07/08	1.5	1.0	3.3	13	0.060	0.070	0.14	0.56
	15/07/08-05/09/08	6.6	6.8	6.8	7.8	0.99	0.74	0.87	0.66
	06/09/08-24/10/08	8.8	5.3	6.6	5.8	0.87	0.96	1.3	0.65
	25/10/08-19/12/08	5.1	3.4	3.9	4.7	0.91	1.7	1.2	0.47
	20/12/08-23/01/09	2.3	2.4	2.3	2.2	2.1	2.9	3.2	3.1
2009	24/01/09-12/03/09	8.0		6.0	13	1.0		1.2	1.8
	13/03/09-17/04/09	9.2	6.4	6.3	8.4	1.3	1.0	0.79	0.76
	18/04/09-21/05/09	6.4	4.7	4.9	6.8	0.51	0.38	0.54	0.41
	22/05/09-22/06/09	7.8	7.6	6.7	8.5	1.2	1.3	1.6	0.97
	23/06/09-24/07/09	3.1	3.4	3.5	5.7	0.40	0.34	0.37	0.40
	25/07/09-24/08/09	2.4	1.9	1.7	3.7	0.16	0.13	0.23	0.54
	25/08/09-1/10/09	4.3	5.6	5.6	8.3	0.70	1.0	1.4	0.56
	2/10/09-2/11/09	8.9	5.9	4.2	7.6	1.4	1.5	1.8	1.5
	3/11/09-11/12/09	2.3	2.3	2.6	3.0	0.44	0.31	0.41	0.71
	12/12/09-15/01/10	2.7	2.5	2.1	3.0	0.81	0.72	0.84	0.55
2010	16/01/10-16/02/10	1.6	3.4	2.3	2.9	0.53	0.43	0.94	0.78
	17/02/10-15/03/10	8.6	7.0	8.5	13	2.4	2.5	2.9	3.4
	16/03/10-22/04/10	4.4	4.9	4.7	7.8	0.49	0.34	0.37	0.62
	23/04/10-25/05/10	15	5.4	6.3	7.9	0.79	0.63	0.72	0.81
	26/05/10-28/06/10	7.3	9.1	7.7	10	1.1	0.94	0.73	1.1
	29/06/10-03/08/10	5.9	6.4	6.7	13	0.36	0.38	0.48	0.53
	04/08/10-01/09/10	5.0	4.8	4.4	4.6	0.56	0.74	0.49	0.42
	02/09/10-08/10/10	5.4	5.9	5.7		0.59	0.55	0.64	
	09/10/10-08/11/10	3.1	2.9	3.1		0.99	1.2	1.2	
	09/11/10-06/12/10	1.5	2.1	2.1		0.69	0.20	0.35	
	07/12/10-17/01/11	2.0	2.5	2.3		0.45	0.47	0.56	

When the ion concentration was below the limit of quantification, the flux was calculated using ½ DL, as suggested by Italian National Institute of Health (ISS)[91].The value was reported in bold and it is just an estimate of the real value.

APPENDIX III: DEPOSITION FLUXES (MG/M2DAY) OF HEAVY METALS AND ARSENIC.

		Aluminum				**Arsenic**			
		µg/m^{2}d							
		Site 1	Site 2	Site 3	Site 4	Site 1	Site 2	Site 3	Site 4
2006	17/01/06-14/02/06	370	270	330	270	7.7	**1.6**	**1.9**	<1.1
	15/02/06-17/03/06	**340**	**240**	**320**	**210**	<8.5	<7.2	**48**	<7.2
	18/03/06-21/04/06	94	**98**	**97**	**850**	<7.2	<6.7	<6.6	<7.1
	22/04/06-12/05/06	61	**190**	200	90	<4.7	<5.1	<6.0	<5.0
	13/05/06-26/05/06	**2600**	**2500**	2200	**2000**	7.1	7.7	44	34
	27/05/06-19/06/06	**410**	**410**	**480**	**630**	13	**14**	13	**15**
	20/06/06-25/07/06	**2900**	2500	2600	2100	**9.5**	**16**	**16**	**19**
	26/07/06-07/09/06	**750**	**1200**	**1300**	**1300**	**17**	<8.7	**1500**	<8.9
	08/09/06-06/10/06	**690**	**340**	**190**	**1200**	<13	<15	**9.7**	3100
	07/10/06-16/11/06	**240**	**210**	**55**	750	<3.4	<7.4	<3.9	<1.6
	17/11/06-20/12/06	**490**	**240**	**490**	**400**	**120**	**18**	**6.7**	**7.7**
	21/12/06-22/01/07	140	170	120	86	<0.60	<0.47	<0.60	<0.65
2007	23/01/07-01/03/07	90	270	130	140	<0.91	<0.82	<0.82	<0.99
	02/03/07-02/04/07	360	640	700	510	<4.7	<4.0	<4.1	<4.5
	03/04/07-08/05/07	160	370	270	380	<0.98	<1.1	<1.1	<1.3
	09/05/07-08/06/07	330	320	240	250	<0.96	<1.4	<0.98	<1.3
	09/06/07-10/07/07	560	540	520	720	<0.46	<0.41	<0.51	<0.50
	11/07/07-09/08/07	7800	1200	1000	1200	<0.97	<0.77	<0.75	<1.2
	10/08/07-10/09/07	2000	2200	2200	1800	<4.2	<3.3	<2.5	<4.6
	11/09/07-19/10/07	860	680		1400	<1.9	<1.7		<1.6
	20/10/07-30/11/07	1400	1600		3100	<3.0	<2.8		<2.1
	1/12/07-19/02/08								
2008	20/02/08-24/03/08	690	830	830	620	<2.3	<2.3	<2.0	<2.3
	25/03/08-04/05/08	**670**	**320**	**330**	**310**	<1.4	<1.4	<1.3	<1.0
	05/05/08-04/06/08	2100	2900	3800	2700	<0.23	<0.19	<0.37	<1.4
	05/06/08-14/07/08	460	300	810	570	<1.3	<1.1	<1.4	<1.2
	15/07/08-05/09/08	1600	1300	1400	1800	**14**	**11**	**11**	**16**
	06/09/08-24/10/08	3700	1100	1300	1200	**20**	**11**	**29**	**23**
	25/10/08-19/12/08	1600	960	800	890	**42**	**44**	**41**	**40**
	20/12/08-23/01/09	380	320	350	340	**16**	**19**	**20**	**42**
2009	24/01/09-12/03/09	2000		1200	1200	<18.1		<17	<21
	13/03/09-17/04/09	1200	**1100**	**450**	**550**	<5.6	<6.3	<5.2	<6.8
	18/04/09-21/05/09	2400	**1200**	**970**	**710**	<9.1	<3.8	<4.4	<5.1
	22/05/09-22/06/09	2100	**820**	**890**	**710**	<20	<9.6	<9.2	<12
	23/06/09-24/07/09	**310**	**550**	**520**	**870**	<7.0	<4.0	<0.96	<5.4
	25/07/09-24/08/09	**1400**	**810**	**840**	**720**	4.8	<1.4	1.9	3.7
	25/08/09-1/10/09	780	890	660	1100	6.5	<5.6	<5.1	<3.6
	2/10/09-2/11/09	3300	1200	220	920	<38	<22	<20	<28
	3/11/09-11/12/09	240	170	210	170	<13	<6.6	<7.4	<8.3
	12/12/09-15/01/10	330	620	330	460	<42	<22	<22	<30
2010	16/01/10-16/02/10	1600	1300	850	1900	<4.6	<6.9	<5.2	<8.1
	17/02/10-15/03/10	4500	4000	5200	5000	<8.6	<7.8	<8.6	<12
	16/03/10-22/04/10	2100	**1700**	1600	**2400**	<3.9	<4.0	<3.5	<4.0
	23/04/10-25/05/10	2100	**1900**	**1600**	3100	<7.3	<6.8	<6.3	<7.5
	26/05/10-28/06/10	2300	2700	2000	2100	<5.6	<6.4	<4.8	<6.6
	29/06/10-03/08/10	870	1100	1200	870	2.5	<1.8	<2.0	4.6
	04/08/10-01/09/10	990	920	950	960	<4.5	<2.6	<2.6	12
	02/09/10-08/10/10	1200	**1500**	1500		40	13	20	
	09/10/10-08/11/10	**1700**	**1700**	**700**		5.9	16	11	
	09/11/10-06/12/10	**460**	**190**	**250**		**23**	49	17	
	07/12/10-17/01/11	110	190	150		5.0	<3.4	2.5	

		Cadmium				**Copper**			
		µg/m^{2}d							
		Site 1	Site 2	Site 3	Site 4	Site 1	Site 2	Site 3	Site 4
2006	17/01/06-14/02/06	**0.71**	**1.5**	**1.8**	<0.056	7.8	8.9	15	8.9
	15/02/06-17/03/06	<0.24	**0.43**	**0.42**	<0.26	<34	<36	<34	<36
	18/03/06-21/04/06	<0.23	<0.24	<0.23	<0.25	<43	<35	<35	<40
	22/04/06-12/05/06	**22**	<0.17	**80**	<0.20	<23	<22	<28	<25
	13/05/06-26/05/06	<0.16	<0.14	**0.13**	**0.28**	**16**	**15**	**14**	**18**
	27/05/06-19/06/06	<0.34	<0.29	<0.30	<0.38	<48	<38	<41	<53
	20/06/06-25/07/06	**0.17**	**0.12**	**0.14**	**0.19**	8.5	**8.1**	11	23
	26/07/06-07/09/06	49	<0.30	<0.22	**0.33**	<45	<43	<31	170
	08/09/06-06/10/06	<0.45	<0.50	<0.48	1.8	<64	<70	<64	<67
	07/10/06-16/11/06	<0.068	**6.0**	**0.090**	<0.068	<8.7	<5.7	<6.1	**9.3**
	17/11/06-20/12/06	0.26	**20**	**0.33**	<0.13	<20	<19	<19	<18
	21/12/06-22/01/07	<0.60	**0.31**	<0.57	<0.62	6.5	5.1	8.3	3.9
2007	23/01/07-01/03/07	**0.54**	**0.48**	<0.76	<0.99	4.3	7.2	9.8	5.5
	02/03/07-02/04/07	<5.0	12	<4.3	<4.7	14	**4.1**	47	8.8
	03/04/07-08/05/07	4.9	**3.0**	**3.9**	<1.3	**2.9**	7.4	10	12
	09/05/07-08/06/07	**2.6**	**1.4**	2.9	**1.4**	16	17	9.0	15
	09/06/07-10/07/07	1.8	**0.85**	1.8	**1.1**	11	10	12	16
	11/07/07-09/08/07	4.9	**3.0**	**3.4**	**1.1**	19	23	19	25
	10/08/07-10/09/07	<4.3	<3.3	<2.5	<4.5	**8.7**	14	16	42
	11/09/07-19/10/07	**1.2**	**3.6**		<1.4	25	20		22
	20/10/07-30/11/07	<2.9	**7.2**		<1.9	24	**5.5**		47
	1/12/07-19/02/08								
2008	20/02/08-24/03/08	<1.2	<1.2	<1.1	<1.2	13	16	23	15
	25/03/08-04/05/08	<0.78	<0.77	<0.66	<0.51	5.6	15	5.3	4.6
	05/05/08-04/06/08	**0.080**	**0.10**	<0.22	<0.71	**4.0**	6.9	13	16
	05/06/08-14/07/08	<0.70	<0.58	<0.61	<0.78	17	20	18	19
	15/07/08-05/09/08	<0.60	<0.46	<0.49	<0.48	16	16	13	24
	06/09/08-24/10/08	1.5	<0.37	<0.97	<0.77	13	13	11	12
	25/10/08-19/12/08	<1.7	<1.5	<1.7	<2.0	17	8.9	11	15
	20/12/08-23/01/09	<0.82	<1.1	<1.0	<2.1	13	12	9.4	29
2009	24/01/09-12/03/09	1.3		1.3	2.1	15		30	23
	13/03/09-17/04/09	<0.10	**0.060**	0.19	0.13	8.8	8.1	8.8	11
	18/04/09-21/05/09	<0.19	**0.070**	**0.070**	**0.080**	6.9	7.0	8.4	9.3
	22/05/09-22/06/09	**0.14**	<0.12	**0.11**	**0.14**	11	11	9.0	11
	23/06/09-24/07/09	<0.080	<0.060	**0.025**	**0.066**	9.8	9.7	8.6	11
	25/07/09-24/08/09	<0.039	<0.022	**0.020**	**0.030**	5.8	5.4	6.5	13
	25/08/09-1/10/09	0.080	0.12	<0.087	**0.050**	6.1	6.3	7.1	14
	2/10/09-2/11/09	**0.22**	<0.23	<0.21	<0.30	**6.0**	**7.1**	**3.9**	8.3
	3/11/09-11/12/09	<0.15	<0.079	<0.086	<0.10	5.6	7.1	5.1	4.0
	12/12/09-15/01/10	<0.43	<0.23	<0.22	<0.32	5.0	**3.5**	13	**20**
2010	16/01/10-16/02/10	0.26	0.30	0.21	0.28	5.0	6.7	6.4	8.7
	17/02/10-15/03/10	0.24	**0.11**	0.23	0.33	7.4	7.0	7.5	8.2
	16/03/10-22/04/10	**0.050**	**0.060**	0.090	<0.057	7.0	4.0	4.9	3.8
	23/04/10-25/05/10	**0.12**	**0.080**	0.24	0.15	7.7	6.0	5.7	6.8
	26/05/10-28/06/10	**0.090**	<0.12	<0.10	0.23	12	12	13	12
	29/06/10-03/08/10	0.36	0.71	0.20	1.3	9.1	14	13	18
	04/08/10-01/09/10	0.29	0.68	0.40	0.22	11	7.6	7.3	12
	02/09/10-08/10/10	0.81	<0.13	4.9		10	8.9	8.6	
	09/10/10-08/11/10	0.14	0.24	0.29		18	7.4	6.4	
	09/11/10-06/12/10	0.20	0.27	<0.16		4.8	6.3	4.8	
	07/12/10-17/01/11	0.050	0.050	0.060		4.3	4.6	5.5	

		Chromium				**Iron**			
		µg/m^{2}d							
		Site 1	Site 2	Site 3	Site 4	Site 1	Site 2	Site 3	Site 4
2006	17/01/06-14/02/06	**2.1**	**1.8**	5.4	**1.6**	310	240	290	330
	15/02/06-17/03/06	**3.4**	**7.0**	3.0	<3.5	320	**230**	**280**	**200**
	18/03/06-21/04/06	**5.9**	**8.9**	**12**	**4.4**	**74**	180	**79**	**490**
	22/04/06-12/05/06	**5.7**	**4.0**	6.9	**1.7**	370	230	190	**2100**
	13/05/06-26/05/06	**6.8**	**7.4**	**3.5**	**2.3**	**2100**	2200	**2000**	**2100**
	27/05/06-19/06/06	**3.4**	<3.4	<4.3	**3.3**	**440**	460	**540**	**1700**
	20/06/06-25/07/06	**2.1**	2.3	**1.9**	**2.4**	120	110	120	680
	26/07/06-07/09/06	<3.9	<4.1	**2.4**	<4.1	130	100	93	140
	08/09/06-06/10/06	<5.5	<6.7	<6.0	**5.5**	**450**	**230**	1300	**730**
	07/10/06-16/11/06	**2.2**	**2.4**	**2.6**	**4.7**	**180**	150	500	**540**
	17/11/06-20/12/06	<1.2	**4.8**	**6.1**	**5.6**	**360**	**160**	400	**290**
	21/12/06-22/01/07	1.7	2.0	**1.0**	**0.74**				
2007	23/01/07-01/03/07	1.3	**1.5**	**1.2**	**1.2**				
	02/03/07-02/04/07								
	03/04/07-08/05/07					**180**	**440**	**440**	**460**
	09/05/07-08/06/07					**490**	**450**	**350**	**310**
	09/06/07-10/07/07					**600**	**590**	**590**	**790**
	11/07/07-09/08/07					6600	**1300**	**1100**	**1100**
	10/08/07-10/09/07					**1900**	**1700**	**890**	**1800**
	11/09/07-19/10/07					**360**	**450**		520
	20/10/07-30/11/07					1100	1100		970
	1/12/07-19/02/08								
2008	20/02/08-24/03/08	**3.1**	**3.4**	**3.3**	**2.7**	1400	1100	2100	1300
	25/03/08-04/05/08	**2.5**	**1.5**	**1.4**	**1.4**	**530**	**270**	**280**	**300**
	05/05/08-04/06/08	**3.6**	**4.7**	**7.7**	**5.0**	1300	1900	2300	1900
	05/06/08-14/07/08	**1.7**	**1.8**	**2.9**	**3.1**	930	730	700	430
	15/07/08-05/09/08	**4.8**	**4.2**	**4.5**	**5.2**	1400	1200	1300	2200
	06/09/08-24/10/08	**9.0**	**3.0**	**4.0**	**4.1**	2300	1400	1100	1100
	25/10/08-19/12/08	**5.7**	**8.8**	**3.8**	**5.1**	1900	870	1100	1200
	20/12/08-23/01/09	**2**	**2**	**2**	<2.6	1400	1100	570	1600
2009	24/01/09-12/03/09	14		14	**12**	3900		3000	1900
	13/03/09-17/04/09	8.8	**6.3**	**4.6**	**5.0**	1300	**1200**	680	**580**
	18/04/09-21/05/09	**9.9**	**5.3**	**6.7**	**5.7**	**1700**	**930**	**1100**	**630**
	22/05/09-22/06/09	**13**	**6.2**	**6.2**	**6.9**	**1500**	**730**	**830**	**660**
	23/06/09-24/07/09	**3.7**	**3.8**	**3.5**	**4.7**	**290**	**470**	**470**	**740**
	25/07/09-24/08/09	**4.9**	**4.4**	**4.1**	**8.0**	**1000**	**650**	**720**	**680**
	25/08/09-1/10/09	**4.1**	**4.5**	**4.1**	**4.0**	680	670	540	440
	2/10/09-2/11/09	**16**	<11.1	<13.8	**8.3**	**1400**	**770**	**360**	**270**
	3/11/09-11/12/09	<7.1	**4.1**	**3.3**	**3.6**	140	180	230	100
	12/12/09-15/01/10	<19	<11	<11	<14	250	290	270	140
2010	16/01/10-16/02/10	**2.5**	**3.2**	**2.9**	**3.2**	240	270	270	280
	17/02/10-15/03/10	**10**	**7.5**	**11**	**11**	2600	1900	2900	2400
	16/03/10-22/04/10	**4.5**	**4.4**	**4.1**	**2.8**	970	900	**890**	550
	23/04/10-25/05/10	**4.8**	**4.6**	**5.0**	**4.5**	**1000**	**850**	1000	810
	26/05/10-28/06/10	**6.3**	**7.5**	**6.4**	**5.7**	**1300**	**1500**	**1200**	**830**
	29/06/10-03/08/10	**2.8**	**4.0**	**3.5**	**4.1**	510	700	570	700
	04/08/10-01/09/10	**4.0**	**2.5**	**3.2**	**3.6**	**660**	**320**	500	550
	02/09/10-08/10/10	<18	<16	<17		800	870	770	
	09/10/10-08/11/10	<9.6	<9.4	<9.4		**260**	230	270	
	09/11/10-06/12/10	<20	<18	<19		130	**130**	100	
	07/12/10-17/01/11	<4.4	<5.8	**3.2**		180	250	220	

		Manganese				**Nickel**			
		µg/m^{2}d							
		Site 1	Site 2	Site 3	Site 4	Site 1	Site 2	Site 3	Site 4
2006	17/01/06-14/02/06	**12**	**8.4**	**14**	**13**	**14**	**1.4**	**2.1**	**1.1**
	15/02/06-17/03/06	24	68	51	21	<7.8	<7.8	<7.2	<7.2
	18/03/06-21/04/06	25	20	27	31	<7.3	<8.1	<8.3	<7.8
	22/04/06-12/05/06	9.6	10	**6.8**	8.0	**4.2**	**8.4**	**44**	<4.9
	13/05/06-26/05/06	54	41	28	22	**5.3**	**4.7**	<3.8	<4.2
	27/05/06-19/06/06	**11**	**7.7**	**7.8**	17	<9.4	<7.4	<8.4	<9.1
	20/06/06-25/07/06	**15**	**13**	**39**	13	**1.8**	4.8	<1.4	<5.0
	26/07/06-07/09/06	**18**	**12**	15	3600	<9.7	<9.4	<6.9	<9.5
	08/09/06-06/10/06	26	21	<15	**18**	<14	<16	<14	<14
	07/10/06-16/11/06	**5.8**	**3.6**	<1.5	**15**	<1.7	<1.4	<1.3	<1.8
	17/11/06-20/12/06	11	8.0	11	8.8	<3.6	<3.9	<3.1	<3.4
	21/12/06-22/01/07	4.1	3.0	3.5	3.1	3.4	0.83	1.5	0.69
2007	23/01/07-01/03/07	5.9	5.9	6.2	5.5	4.9	1.4	1.5	**0.90**
	02/03/07-02/04/07	20	19	21	20	<5.6	<4.6	<5.1	<5.3
	03/04/07-08/05/07	6.4	10	18	14	2.7	**1.9**	**2.8**	3.3
	09/05/07-08/06/07	7.2	7.9	7.3	7.7	2.5	**1.8**	**1.3**	**2.0**
	09/06/07-10/07/07	7.2	5.3	7.4	**5.1**	2.7	4.1	**2.2**	**3.7**
	11/07/07-09/08/07	17	11	7.1	19	11	4.9	**3.9**	**5.2**
	10/08/07-10/09/07	18	**8.4**	9.7	**16**	**5.8**	**5.9**	**4.6**	**6.9**
	11/09/07-19/10/07	**2.8**	4.9		**7.6**	**2.0**	<2.2		**5.4**
	20/10/07-30/11/07	4.5	11		**4.1**	<3.6	**3.2**		**5.6**
	1/12/07-19/02/08								
2008	20/02/08-24/03/08	16	20	20	16	**2.9**	**2.8**	**2.8**	**2.7**
	25/03/08-04/05/08	**12**	12	**7.2**	**8.5**	**2.7**	**1.5**	**1.4**	**1.3**
	05/05/08-04/06/08	24	**37**	44	**35**	**2.7**	5.2	4.8	**3.5**
	05/06/08-14/07/08	16	36	33	19	**1.6**	**1.3**	**4.4**	**3.1**
	15/07/08-05/09/08	35	**30**	**35**	36	**4.0**	**3.0**	**3.6**	**3.8**
	06/09/08-24/10/08	48	27	28	**28**	**6.3**	**2.4**	**3.5**	**6.3**
	25/10/08-19/12/08	30	18	18	17	<7.7	<6.0	<6.5	<7.3
	20/12/08-23/01/09	8.5	12	12	22	<3.6	<4.0	<3.8	<4.1
2009	24/01/09-12/03/09	38.82		38	30	<10		<10	<11
	13/03/09-17/04/09	34	25	19	16	4.7	<4.1	<3.1	**5.8**
	18/04/09-21/05/09	48	25	29	19	**5.2**	**2.5**	**3.1**	**3.0**
	22/05/09-22/06/09	46	21	26	22	**6.3**	**3.5**	**3.2**	**3.7**
	23/06/09-24/07/09	11	7.1	13	18	<4.1	<2.8	1.4	**2.4**
	25/07/09-24/08/09	22	14	19	28	**2.2**	**1.7**	**4.1**	**1.9**
	25/08/09-1/10/09	27	27	23	22	**2.0**	**1.8**	**2.5**	**1.3**
	2/10/09-2/11/09	53	30	20	17	**7.4**	<6.0	<4.8	<6.3
	3/11/09-11/12/09	18	9.2	11	7.7	<3.0	<1.7	<2.0	<1.8
	12/12/09-15/01/10	23	13	12	26	<9.0	<5.2	<5.1	<6.5
2010	16/01/10-16/02/10	11	14	12	22	<3.0	<4.5	<3.4	<4.6
	17/02/10-15/03/10	64	44	62	55	**5.0**	**4.4**	**5.2**	**5.8**
	16/03/10-22/04/10	22	22	21	14	**2.3**	**2.4**	**2.2**	**2.1**
	23/04/10-25/05/10	26	20	27	25	**3.6**	<4.6	**3.1**	<5.1
	26/05/10-28/06/10	27	37	28	23	**5.0**	**4.0**	**3.3**	6.0
	29/06/10-03/08/10	15	20	17	17	1.7	**2.1**	2.6	3.7
	04/08/10-01/09/10	31	14	15	18	**2.0**	<2.4	**1.8**	**2.1**
	02/09/10-08/10/10	18	18	19		**4.3**	<5.4	<5.6	
	09/10/10-08/11/10	9.0	7.3	9.9		<3.0	<3.0	<2.8	
	09/11/10-06/12/10	4.9	4.6	4.2		<6.4	<6.0	<6.0	
	07/12/10-17/01/11	5.6	6.7	6.4		**1.1**	<2.0	**1.1**	

		Lead				**Zinc**			
		µg/m^{2}d							
		Site 1	Site 2	Site 3	Site 4	Site 1	Site 2	Site 3	Site 4
2006	17/01/06-14/02/06	9.8	5.8	9.4	22	91	35	40	56
	15/02/06-17/03/06	34	28	30	43	**18**	63	84	960
	18/03/06-21/04/06	**20**	**17**	**40**	<22	130	80	74	150
	22/04/06-12/05/06	90	**19**	42	17	62	56	210	120
	13/05/06-26/05/06	**61**	**12**	<7.8	<8.8	130	160	26	72
	27/05/06-19/06/06	**37**	<20	**46**	200	110	81	82	67
	20/06/06-25/07/06	**7.5**	<4.1	<3.7	<10	12	**8.1**	**8.6**	**12**
	26/07/06-07/09/06	**29**	120	43	**130**	43	42	47	190
	08/09/06-06/10/06	<31	210	800	**170**	65	38	72	60
	07/10/06-16/11/06	**5.2**	**73**	**72**	250	8.3	6.7	**10**	100
	17/11/06-20/12/06	170	**120**	**150**	**160**	200	**18**	51	36
	21/12/06-22/01/07	12	4.2	5.6	3.2	110	16	29	19
2007	23/01/07-01/03/07	9.1	6.4	5.8	4.1	50	22	48	37
	02/03/07-02/04/07	19	24	14	<5.9	76	190	120	<60
	03/04/07-08/05/07	6	9	8	4	40	**19**	**31**	**28**
	09/05/07-08/06/07	16	22	6.3	13	76	130	53	63
	09/06/07-10/07/07	16	20	26	22	23	28	28	35
	11/07/07-09/08/07	34	12	20	28	160	41	44	56
	10/08/07-10/09/07	25	22	22	72	360	70	70	420
	11/09/07-19/10/07	74	7.0		26	41	55		43
	20/10/07-30/11/07	41	9.0		130	220	65		160
	1/12/07-19/02/08								
2008	20/02/08-24/03/08	**12**	**12**	**33**	**11**	59	59	57	50
	25/03/08-04/05/08	**7.3**	**4.8**	**11**	**3.8**	**12**	41	**8.2**	**6.6**
	05/05/08-04/06/08	**8.9**	**19**	36	**11**	17	20	33	35
	05/06/08-14/07/08	**5.7**	**3.5**	**7.1**	**7.4**	76	26	100	22
	15/07/08-05/09/08	**17**	**14**	**19**	**26**	44	31	40	150
	06/09/08-24/10/08	**13**	14	**18**	**17**	60	48	77	51
	25/10/08-19/12/08	**19**	<22	**21**	<27	90	50	59	100
	20/12/08-23/01/09	<12	<18	<16	<16	55	55	31	250
2009	24/01/09-12/03/09	17		24	35	110		120	150
	13/03/09-17/04/09	7.7	**9.7**	14	10	29	25	50	**11**
	18/04/09-21/05/09	**12**	**11**	**8.4**	**6.3**	**21**	**19**	23	**17**
	22/05/09-22/06/09	**15**	**15**	**18**	**11**	42	**20**	**16**	**19**
	23/06/09-24/07/09	**15**	**10**	**9.6**	**11**	**12**	**14**	**13**	**27**
	25/07/09-24/08/09	11	**6.0**	**10**	**8.9**	16	11	15	18
	25/08/09-1/10/09	**4.1**	**4.5**	**4.1**	**4.0**	19	19	23	20
	2/10/09-2/11/09	**16**	**8.8**	<11	<14	110	130	64	64
	3/11/09-11/12/09	<7.1	**4.1**	**3.3**	**3.6**	29	26	18	37
	12/12/09-15/01/10	<19	<11	<11	<14	75	37	26	54
2010	16/01/10-16/02/10	11	45	11	18	52	95	79	120
	17/02/10-15/03/10	**16**	**26**	**17**	**19**	30	42	55	62
	16/03/10-22/04/10	**6.3**	**8.8**	**6.2**	**3.1**	30	42	55	62
	23/04/10-25/05/10	**29**	**13**	**13**	**5.9**	29	47	69	44
	26/05/10-28/06/10	**21**	**20**	**18**	**9.1**	93	65	30	140
	29/06/10-03/08/10	**4.6**	**6.1**	**8.6**	**7.9**	29	29	26	71
	04/08/10-01/09/10	**19**	**13**	**7.9**	**8.1**	25	42	29	34
	02/09/10-08/10/10	**21**	**20**	**16**		140	84	58	
	09/10/10-08/11/10	**11**	**3.9**	**9.3**		78	110	110	
	09/11/10-06/12/10	**5.8**	**5.0**	13		110	410	84	
	07/12/10-17/01/11	**3.3**	**3.5**	**3.0**		45	49	34	

For each data, when both the soluble and insoluble values were below the detection limit, the flux was calculated by using the detection limit and the data was reported as "lower then". When only one fraction (soluble or insoluble) was below the detection limit, the fraction which makes the highest contribution to the total flux was considered. If it were the fraction below the detection limit, the flux was calculated by using the detection limit and the data was reported as "lower then". If it were the other, flux was calculated by using ½ DL, as suggested by Italian National Institute of Health (ISS)[91]. The value is reported in bold and it is just an estimate of the real value

APPENDIX IV: AIR CONCENTRATIONS OF PM2.5 AND OF ITS COMPONENTS

Date	Wind direction	$PM_{2.5}$	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-	SO_4^{2-}
		ug/m^3								
29/11-2/12/11	calm	77	0.10	9.0	0.45	0.14	*0.05*	0.36	25	3
	inland	65								
3-4/12/11	inland	21	0.15	2.53	0.22	0.11	*0.04*	0.49	5.4	2
3-7/12/11	calm	42	0.23	4.10	0.45	0.13	*0.05*	0.9	11	2
5-7/12/11	inland	24	0.11	2.80	0.17	0.08	*0.04*	0.48	6.9	1.6
10-11/12/11	calm	86	0.10	6.9	0.58	0.10	*0.04*	1.7	20	3
	coast	90	0.11	5.7	0.36	0.06	*0.05*	0.9	15	3
17-18/12/11	coast	12	0.11	0.35	0.04	0.07	*0.05*	0.13	1.0	0.3
	calm	11	0.08	0.51	0.13	0.12	*0.05*	0.11	1.7	0.3
19-21/12/11	coast	12	0.18	0.95	0.07	0.09	*0.05*	0.22	2.7	0.7
	calm	32	0.07	1.61	0.20	0.17	*0.04*	0.19	5.4	0.8
31/12/11-1/1/12	calm	40	0.06	3.04	1.1	*0.04*	0.16	0.48	10	1.4
31/12/11-4/1/12	coast	23	0.10	1.92	0.67	0.10	0.15	0.42	5.9	1.3
3-5/1/12	calm	27	0.05	1.90	0.15	0.06	*0.05*	0.14	5.1	0.8
10-11/1/12	inland	23	0.08	2.14	0.26	0.10	*0.03*	0.18	6.3	0.7
	calm	29	0.12	2.01	0.27	0.12	*0.05*	0.41	6.5	0.8
14-15/1/12	calm	64	0.07	5.8	0.30	0.05	*0.05*	0.60	17	2
	inland	57	*0.06*	4.5	0.24	*0.08*	*0.04*	0.38	15	2.0
17-19/1/12	calm	34	0.11	2.07	0.32	0.17	*0.03*	0.63	6.3	1.5
	coast	27	*0.056*	1.80	0.21	*0.08*	*0.04*	0.38	4.8	1.3
21-22/1/12	coast	64	*0.08*	5.7	0.40	*0.16*	*0.07*	0.8	16	3
25-26/1/12	calm	20	0.13	1.44	0.15	*0.11*	*0.04*	0.25	4.2	1.2
	inland	25	0.08	2.25	0.15	0.14	*0.03*	0.20	6.7	1.6
28-19/1/12	calm	39	*0.07*	3.93	0.27	*0.11*	*0.04*	0.64	11	3
	inland	34	0.16	3.27	0.36	*0.12*	*0.05*	0.47	7.8	3
1-2/2/12	coast	17	0.28	0.91	0.17	*0.16*	*0.07*	0.8	0.3	3
11-12/2/12	coast	31	0.29	2.16	0.23	*0.08*	*0.07*	0.15	0.3	7
18-19/2/12	calm	43	0.13	3.91	0.22	0.15	*0.05*	0.33	13	1.7
25-26/2/12	calm	32	*0.07*	0.88	0.12	*0.06*	*0.01*	0.46	6.2	1.4
29/2-1/3/12	calm	40	0.25	1.03	*0.05*	0.27	*0.01*	0.24	8.8	2
3-4/3/12	calm	52	*0.031*	1.95	*0.05*	*0.05*	*0.005*	0.36	16	3
	inland	48	0.12	4.01	0.22	0.15	0.13	0.31	11	3
7-8/3/12	inland	42	0.17	3.60	0.23	0.18	0.14	0.36	9.1	2
	calm	41	*0.07*	1.81	0.14	0.16	0.12	0.43	8.5	2
10-13/3/12	calm	26	0.10	0.85	*0.06*	0.16	*0.01*	0.09	3.2	1.6
	coast	25	0.11	0.52	0.07	0.10	0.09	0.17	3.4	1.7
14-15/3/12	calm	25	0.042	2.42	*0.04*	0.13	*0.04*	0.16	6.5	2.0
18-19/3/12	calm	31	0.12	1.96	*0.06*	0.18	*0.06*	0.47	3.1	4
	coast	31	0.29	1.88	0.36	0.27	*0.09*	0.40	2.6	4

21-23/3/12	calm	31	0.06	2.94	0.21	0.11	*0.04*	0.17	7.6	3
	inland	29	0.08	2.41	0.15	0.15	*0.05*	0.18	6.1	2
24-25/3/12	calm	53	0.06	3.72	0.49	0.13	*0.04*	0.15	7.6	5
	inland	41	0.07	3.01	0.36	0.17	*0.05*	0.25	6.6	4
26-28/3/12	calm	19	0.03	1.53	*0.06*	0.17	*0.06*	*0.10*	2.9	2
	coast	24	0.04	1.00	0.06	0.15	*0.06*	0.11	3.2	3
31/3-1/4/12	calm	21	0.08	1.20	0.11	0.21	*0.05*	0.23	2.0	2
	coast	26	0.27	1.22	0.08	0.24	0.06	0.40	2.2	2
3-4/4/12	calm	32	0.05	2.92	0.16	0.09	*0.04*	0.43	6.8	2
	inland	35								
8-12/4/12	calm	14	0.047	0.93	0.06	0.08	*0.04*	0.05	2.0	1.2
	inland	12	0.08	0.70	0.05	0.06	*0.024*	0.11	1.5	1.0
14-15/4/12	calm	18	0.018	0.84	*0.05*	0.09	*0.05*	*0.08*	1.1	1.5
	coast	14	0.10	0.95	*0.09*	0.12	*0.09*	0.13	1.2	1.6
17-18/4/12	calm	13	0.05	0.66	0.05	0.09	*0.05*	*0.08*	1.1	1.1
	coast	12	0.10	0.47	*0.05*	0.11	*0.05*	*0.08*	0.8	0.9
21-22/4/12	calm	21	0.11	0.31	*0.05*	0.14	*0.05*	0.08	0.5	0.9
	inland	8.1	0.13	0.23	*0.03*	0.05	0.04	0.05	0.32	0.9
24-25/4/12	calm	18	0.10	0.26	0.06	0.15	*0.06*	*0.09*	0.3	0.9
	inland	8.6	0.12	0.19	0.03	0.13	*0.03*	0.07	0.37	0.7
27-28/4/12	calm	25	0.09	1.55	0.15	*0.07*	*0.07*	*0.10*	2.7	2

Date	**Wind direction**	**OC**	**EC**	**Lvg**	**Fe**	**Zn**	**Cd**	**Pb**	**Cu**	**Ni**
		µg/m^3					ng/m^3			
29/11-2/12/11	calm	20	1.5	0.578	0.17	0.05	0.23	17	7.0	3.3
	inland									
3-4/12/11	inland	6.4	0.9	0.302	0.07	0.08	0.14	9.4	6.2	2.6
3-7/12/11	calm	16	1.4	0.476	0.12	0.031	0.18	11	6.2	2.8
5-7/12/11	inland	6.8	1.1	0.330	0.08	0.04	0.17	10	6.1	2.2
10-11/12/11	calm	22	2.2	1.008	0.16	0.11	0.42	15	8.7	3.2
	coast	15	1.5	0.923	0.16	0.15	0.44	32	13	4.6
17-18/12/11	coast	11	0.6	0.244	*0.09*	0.08	0.09	9	9	3.0
	calm	8.3	0.7	0.128	0.08	*0.024*	0.04	2.4	3.0	2.8
19-21/12/11	coast	5.5	0.9	0.278	0.08	0.07	0.10	9	9	3.3
	calm	9.0	2.1	0.480	0.11	*0.020*	0.08	10	6.6	2.1
31/12/11-1/1/12	calm	8.4	1.5	0.672	0.07	*0.013*	0.10	14	30	1.1
31/12/11-4/1/12	coast	7.3	1.4	0.452	0.08	0.07	0.13	13	27	2.4
3-5/1/12	calm	6.5	0.7	0.017	0.04	0.038	0.15	2.7	2.3	1.5
10-11/1/12	inland	7.1	1.2	0.437	0.07	0.07	0.12	8.5	6.3	2.0
	calm	7.4	1.5	0.484	0.09	0.021	0.11	6.1	5.0	1.4
14-15/1/12	calm	11	1.0	0.422	0.17	*0.016*	0.043	11	5.7	3.2
	inland	4.9	6	0.789	0.07	0.08	0.16	10	5.6	1.9

17-19/1/12	calm	11	1.2	0.601	0.16	*0.019*	0.17	8.8	3.2	1.8
	coast	8.6	1.6	0.604	0.05	0.06	0.16	11	4.2	3.3
21-22/1/12	coast	17	1.2	1.788	0.28	*0.05*	0.26	26	9	4.1
25-26/1/12	calm	5.3	0.8	0.243	0.32	*0.019*	0.05	7.8	2.8	2.5
	inland	6.2	0.7	0.328	1.36	0.03	0.10	19	3.6	3.5
28-19/1/12	calm	9.1	0.7	0.4260	0.10	*0.012*	0.12	8.2	2.5	1.6
	inland	6.9	3.5	0.564	0.83	*0.03*	0.15	13	6.1	3.5
1-2/2/12	coast	6.2	0.23	0.129	0.18	0.06	0.11	9	4.5	6
11-12/2/12	coast	7.2	0.35	0.216	0.82	*0.04*	0.19	12	4.8	5
18-19/2/12	calm	6.3	0.9	0.222	0.08	0.014	0.16	9.7	4.1	3.1
25-26/2/12	calm	6.7	1.2	0.314	0.07	*0.012*	0.08	5.7	2.6	2.6
29/2-1/3/12	calm	7.7	1.3	0.350	0.07	*0.016*	0.12	6.8	3.0	2.1
3-4/3/12	calm	9.2	0.9	0.272	0.08	*0.014*	0.23	7.9	3.0	2.1
	inland	6.2	0.6	0.234	0.19	*0.03*	0.19	9	6.3	2.3
7-8/3/12	inland	7.3	0.7	0.222	0.10	*0.03*	0.20	10	4.7	1.5
	calm	9.2	0.9	0.304	0.10	0.019	0.19	9.0	3.7	1.9
10-13/3/12	calm	8.3	1.6	0.310	0.16	*0.04*	0.16	4.8	6	3.9
	coast	4.7	0.7	0.175	0.07	*0.024*	0.19	5.6	5.1	2.2
14-15/3/12	calm	6.8	1.1	0.139	0.09	*0.013*	0.08	5.3	2.0	0.9
18-19/3/12	calm	9	2.0	0.231	0.08	*0.015*	0.11	5.0	2.8	2.0
	coast	7.0	0.7	0.149	*0.13*	*0.06*	0.15	10	6	3.6
21-23/3/12	calm	7.4	1.0	0.20	0.10	*0.013*	0.17	10.0	4.1	1.3
	inland	7.4	1.1	0.153	0.15	*0.03*	0.12	9	6.4	2.3
24-25/3/12	calm	14	1.4	0.288	0.10	*0.017*	0.20	16	3.1	2.4
	inland	6.1	5	0.403	0.08	*0.03*	0.21	17	4.8	2.6
26-28/3/12	calm	4.4	1.1	0.082	0.1	*0.020*	0.07	13	3.2	1.4
	coast	4.8	0.7	0.113	0.09	*0.04*	0.15	11	5.4	2.3
31/3-1/4/12	calm	5.4	0.8	0.15	0.17	*0.03*	0.05	2.6	2.1	2.4
	coast	3.1	0.4	0.063	0.11	*0.04*	0.06	3.9	5.0	2.3
3-4/4/12	calm	7.0	0.9	0.135	0.09	*0.013*	0.10	8.4	4.2	1.6
	inland									
8-12/4/12	calm	2.4	0.6	0.083	0.12	*0.011*	0.032	2.7	4.1	1.0
	inland	1.9	0.40	0.073	0.09	*0.016*	0.038	4.7	4.2	1.5
14-15/4/12	calm	3.5	0.5	0.138	0.04	*0.013*	0.022	1.0	0.9	1.1
	coast	4.4	0.22	0.072	*0.13*	*0.06*	*0.06*	4	4	2.6
17-18/4/12	calm	2.4	0.8	0.116	0.04	*0.015*	0.025	1.9	1.8	1.0
	coast	2.0	0.35	0.043	0.07	*0.03*	*0.03*	3.0	17	1.5
21-22/4/12	calm	2.5	0.24	0.053	0.08	*0.03*	*0.04*	1.5	2.9	2.4
	inland	1.3	0.12	0.016	0.04	*0.017*	*0.019*	2.2	2.7	1.0
24-25/4/12	calm	2.2	0.5	0.037	0.09	*0.017*	0.033	1.5	2.4	2.1
	inland	1.3	0.28	0.022	0.04	*0.018*	0.025	1.9	1.8	1.0
27-28/4/12	calm	4.9	1.1	0.098	0.11	*0.013*	0.08	7.5	4.2	2.4

Date	Wind direction	Flu	Pir	B(a)A	Cri	B(b)F	B(k)F	B(a)P	D(a,h)A	B(g,h,i)P	I(1,2,3)P
		ng/m^3									
29/11-2/12/11	calm	0.36	0.46	0.25	0.53	0.8	0.30	0.45	0.13	0.64	0.33
	inland	0.34	0.45	0.20	0.45	0.8	0.29	0.39	0.12	0.62	0.38
3-4/12/11	inland	0.14	0.20	0.17	0.25	0.5	0.20	0.31	0.09	0.45	0.21
3-7/12/11	calm	0.27	0.37	0.31	0.50	0.9	0.33	0.52	0.18	0.70	0.67
5-7/12/11	inland	0.20	0.29	0.20	0.34	0.6	0.23	0.34	0.12	0.48	0.48
10-11/12/11	calm	0.73	1.2	0.99	1.27	2	0.82	1.5	0.44	1.65	1.62
	coast										
17-18/12/11	coast	0.24	0.32	0.17	0.27	0.4	0.16	0.25	0.08	0.33	0.33
	calm	0.43	0.5	0.24	0.37	0.4	0.20	0.31	0.09	0.36	0.75
19-21/12/11	coast	0.44	0.55	0.28	0.40	0.5	0.21	0.38	0.11	0.45	0.36
	calm	0.96	1.3	0.69	0.95	1.1	0.42	0.87	0.23	0.88	0.71
31/12/11-1/1/12	calm	0.39	0.64	0.32	0.57	0.9	0.32	0.53	0.18	0.70	0.59
31/12/11-4/1/12	coast	0.28	0.34	0.24	0.41	0.7	0.27	0.43	0.13	0.58	0.56
3-5/1/12	calm	0.28	0.33	0.20	0.35	0.5	0.19	0.31	0.09	0.45	0.36
10-11/1/12	inland	0.38	0.50	0.35	0.55	0.8	0.30	0.59	0.13	0.67	0.53
	calm	0.51	0.64	0.38	0.57	0.7	0.29	0.57	0.12	0.66	0.53
14-15/1/12	calm	0.49	0.58	0.43	0.68	0.9	0.32	0.59	0.14	0.71	0.62
	inland	0.44	0.55	0.41	0.67	0.9	0.33	0.61	0.14	0.74	0.68
17-19/1/12	calm	0.74	1.0	0.86	1.11	1.2	0.43	0.76	0.25	0.80	1.16
	coast	0.58	0.79	0.75	0.98	1.1	0.39	0.69	0.23	0.62	0.89
21-22/1/12	coast	1.0	1.5	1.21	1.54	2.0	0.73	1.3	0.42	1.28	1.8
25-26/1/12	calm	0.33	0.44	0.21	0.38	0.5	0.18	0.29	0.10	0.32	0.47
	inland	0.26	0.37	0.20	0.38	0.6	0.21	0.31	0.12	0.43	0.54
28-19/1/12	calm	0.36	0.45	0.31	0.59	0.8	0.30	0.42	0.17	0.53	0.73
	inland	0.40	0.5	0.30	0.65	1.0	0.36	0.46	0.21	0.62	0.90
1-2/2/12	coast	0.36	0.39	0.14	0.27	0.4	0.14	0.17	0.09	0.29	0.29
11-12/2/12	coast	1.3	1.2	0.33	0.66	1.0	0.31	0.36	0.18	0.53	0.59
18-19/2/12	calm	0.20	0.26	0.12	0.24	0.5	0.16	0.21	0.09	0.36	0.28
25-26/2/12	calm	0.21	0.29	0.19	0.35	0.6	0.21	0.34	0.12	0.48	0.36
29/2-1/3/12	calm	0.18	0.24	0.14	0.27	0.5	0.19	0.31	0.11	0.44	0.33
3-4/3/12	calm	0.16	0.22	0.12	0.24	0.5	0.17	0.24	0.10	0.39	0.28
	inland	0.16	0.20	0.10	0.21	0.4	0.15	0.19	0.10	0.34	0.29
7-8/3/12	inland	0.44	0.47	0.18	0.38	0.6	0.21	0.29	0.11	0.43	0.36
	calm	0.5	0.5	0.19	0.4	0.59	0.21	0.3	0.11	0.4	0.3
10-13/3/12	calm	0.4	0.5	0.22	0.5	0.66	0.25	0.4	0.13	0.5	0.4
	coast	0.19	0.20	0.09	0.18	0.29	0.11	0.15	0.06	0.22	0.18
14-15/3/12	calm	0.22	0.3	0.14	0.3	0.48	0.18	0.3	0.11	0.4	0.3
18-19/3/12	calm	0.17	*0.24*	0.18	0.6	0.72	0.3	0.4	0.17	0.6	0.4
	coast	*0.17*	*0.3*	0.13	0.3	0.46	0.18	0.19	0.12	0.4	0.3

21-23/3/12	calm	0.14	0.18	0.11	0.23	0.39	0.14	0.22	0.08	0.3	0.20
	inland	0.13	0.18	0.09	0.18	0.32	0.12	0.16	0.08	0.3	0.21
24-25/3/12	calm	0.18	0.17	0.16	0.6	0.90	0.3	0.3	0.21	0.7	0.3
	inland	0.14	*0.13*	0.15	0.4	0.75	0.25	0.2	0.17	0.6	0.3
26-28/3/12	calm	0.16	0.17	0.09	0.20	0.27	0.10	0.14	0.06	0.21	0.13
	coast	0.16	*0.15*	0.06	0.15	0.20	0.08	0.09	0.05	0.15	0.12
31/3-1/4/12	calm	0.11	*0.18*	0.06	0.16	0.20	0.08	0.10	*0.05*	0.16	0.09
	coast	*0.09*	*0.18*	*0.03*	0.06	0.09	0.03	0.04	*0.05*	0.07	*0.06*
3-4/4/12	calm	*0.05*	*0.08*	0.02	0.05	0.11	0.04	0.04	0.024	0.08	0.06
	inland	*0.09*	*0.18*	0.063	0.14	0.29	0.10	0.09	0.07	0.22	0.18
8-12/4/12	calm	0.04	*0.07*	0.05	0.10	0.22	0.07	0.08	0.05	0.17	0.09
	inland	0.04	*0.07*	0.014	0.022	0.05	0.017	0.018	*0.021*	0.04	0.03
14-15/4/12	calm	*0.11*	*0.17*	0.07	0.13	0.26	0.09	0.10	*0.05*	0.20	0.13
	coast	*0.07*	*0.13*	*0.025*	*0.04*	0.07	0.03	0.03	*0.04*	0.06	0.04
17-18/4/12	calm	0.05	0.10	0.020	0.04	0.08	0.03	0.03	0.03	0.07	0.05
	coast	*0.07*	*0.14*	*0.03*	0.04	0.09	0.03	0.03	*0.04*	0.08	*0.06*
21-22/4/12	calm	*0.08*	*0.16*	*0.03*	*0.05*	0.06	*0.07*	*0.03*	*0.04*	*0.05*	*0.05*
	inland										
24-25/4/12	calm	*0.09*	*0.16*	*0.03*	0.06	0.07		0.03	*0.05*	0.06	*0.05*
	inland	*0.04*	*0.07*	*0.014*	0.03	0.05	0.015	0.022	*0.021*	0.04	*0.025*
27-28/4/12	calm	*0.07*	*0.13*	0.04	0.08	0.13	0.04	0.05	*0.04*	0.11	0.05

*blue cells: missing data

orange cells: below method quantification limit data. Air concentration has been calculated by using the method quantification limit. The value represents the upper limit for the component air concentration.

APPENDIX V: G MATRIX, FACTOR CONTRIBUTION TO PM2.5

d-m-yy hh.mm	Sodium	Regional transport	NO_x conversion	Vehicular traffic
11/2/11 16.00	0.03	1.08	1.20	0.69
11/2/11 17.00	0.03	1.04	1.00	1.01
11/2/11 18.00	0.04	1.06	0.94	1.41
11/2/11 19.00	0.05	1.20	0.78	2.29
11/2/11 20.00	0.03	1.15	0.48	0.94
11/2/11 21.00	0.03	1.11	0.44	1.00
11/2/11 22.00	0.03	1.11	0.43	0.69
11/2/11 23.00	0.03	1.10	0.41	0.76
12/2/11 0.00	0.03	1.06	0.40	0.61
12/2/11 1.00	0.03	1.03	0.34	0.70
12/2/11 2.00	0.03	1.06	0.39	0.83
12/2/11 3.00	0.03	1.05	0.37	0.83
12/2/11 4.00	0.03	1.05	0.40	0.83
12/2/11 5.00	0.03	1.03	0.42	0.91
12/2/11 6.00	0.03	1.07	0.34	1.03
12/2/11 7.00	0.03	1.04	0.32	0.94
12/2/11 8.00	0.03	0.99	0.32	1.23
12/2/11 9.00	0.03	1.00	0.60	1.26
12/2/11 10.00	0.05	1.19	0.92	0.92
12/2/11 11.00	0.09	1.12	0.85	0.54
12/2/11 12.00	0.05	1.05	0.55	0.53
12/2/11 13.00	0.04	1.03	0.44	0.62
12/2/11 14.00	0.03	1.01	0.46	0.50
12/2/11 15.00	0.03	0.99	0.47	0.50
12/2/11 16.00	0.05	0.99	0.46	0.52
12/2/11 17.00	0.09	0.98	0.37	0.82
12/2/11 18.00	0.13	1.03	0.19	0.77
12/2/11 19.00	0.12	0.94	0.21	1.18
12/2/11 20.00	0.04	1.02	0.44	1.13
12/2/11 21.00	0.03	1.17	0.73	0.82
12/2/11 22.00	0.10	1.20	1.21	0.86
12/2/11 23.00	0.11	1.25	2.41	0.70
13/2/11 0.00	0.10	1.22	3.08	0.75
13/2/11 1.00	0.08	1.20	3.44	0.61
13/2/11 2.00	0.02	1.21	3.47	0.67
13/2/11 3.00	0.02	1.23	3.89	0.59
13/2/11 4.00	0.06	1.27	3.91	0.51
13/2/11 5.00	0.06	1.14	3.93	0.59
13/2/11 6.00	0.07	1.11	4.41	0.68
13/2/11 7.00	0.02	1.24	4.51	0.53
13/2/11 8.00	0.05	1.16	4.53	0.53
13/2/11 9.00	0.02	1.13	4.93	0.78
13/2/11 10.00	0.02	1.19	4.97	0.54
13/2/11 11.00	0.02	1.31	5.08	0.54
13/2/11 12.00	0.02	1.39	5.02	0.76
13/2/11 13.00	0.02	1.42	4.82	0.50
13/2/11 14.00	0.02	1.43	4.96	0.28
13/2/11 15.00	0.02	1.48	4.96	0.25
13/2/11 16.00	0.02	1.44	5.17	0.32
13/2/11 17.00	0.02	1.49	5.21	0.27
13/2/11 18.00	0.02	1.45	5.11	0.45
13/2/11 19.00	0.02	1.39	4.95	0.75
13/2/11 20.00	0.02	1.48	5.37	0.79
13/2/11 21.00	0.02	1.55	4.83	0.66
13/2/11 22.00	0.02	1.40	4.69	1.11
13/2/11 23.00	0.05	1.37	4.75	1.11
14/2/11 0.00	0.05	1.27	4.46	0.99
14/2/11 1.00	0.05	1.28	4.34	1.04

d-m-yy hh.mm	Sodium	Regional transport	NO_x conversion	Vehicular traffic
14/2/11 2.00	0.03	1.27	4.18	1.02
14/2/11 3.00	0.02	1.27	4.05	0.86
14/2/11 4.00	0.02	1.27	4.01	0.93
14/2/11 5.00	0.02	1.32	3.94	0.96
14/2/11 6.00	0.02	1.37	3.93	1.05
14/2/11 7.00	0.02	1.35	3.69	0.91
14/2/11 8.00	0.02	1.40	3.81	0.98
14/2/11 9.00	0.02	1.51	3.89	0.99
14/2/11 12.00	1.77	1.66	4.62	0.91
14/2/11 13.00	1.40	1.73	4.84	0.73
14/2/11 14.00	1.49	1.75	4.79	0.33
14/2/11 15.00	1.26	1.56	4.74	0.36
14/2/11 16.00	1.42	1.56	4.63	0.14
14/2/11 17.00	1.47	1.52	5.00	0.19
14/2/11 18.00	1.17	1.46	5.07	0.35
14/2/11 19.00	1.41	1.54	5.08	0.33
14/2/11 20.00	1.76	1.91	5.15	0.17
14/2/11 21.00	1.16	2.03	5.24	0.10
14/2/11 22.00	1.29	1.95	5.34	0.21
14/2/11 23.00	1.80	1.89	5.34	0.23
15/2/11 0.00	1.49	1.91	5.24	0.45
15/2/11 1.00	1.25	1.94	5.24	0.37
15/2/11 3.00	1.39	1.80	5.25	0.27
15/2/11 4.00	1.45	1.61	5.07	0.23
15/2/11 5.00	1.42	1.59	5.02	0.25
15/2/11 7.00	1.25	1.52	4.23	0.78
15/2/11 8.00	1.75	1.51	4.56	0.61
15/2/11 9.00	1.50	1.67	4.26	0.39
15/2/11 10.00	1.29	1.69	3.71	0.52
15/2/11 11.00	1.65	1.76	4.33	0.39
15/2/11 12.00	1.58	1.65	4.53	0.06
15/2/11 13.00	2.01	1.68	4.27	0.02
15/2/11 14.00	1.42	1.66	4.13	0.25
15/2/11 15.00	1.79	1.44	3.07	0.15
15/2/11 16.00	1.38	1.43	2.74	0.33
15/2/11 17.00	1.34	1.10	1.82	0.48
15/2/11 18.00	1.24	1.05	1.71	0.53
15/2/11 19.00	1.52	1.07	1.82	0.84
15/2/11 20.00	1.52	1.22	1.95	0.61
15/2/11 21.00	1.52	1.12	2.18	0.39
15/2/11 22.00	1.53	1.12	2.15	0.39
15/2/11 23.00	1.37	1.26	2.23	0.46
16/2/11 0.00	1.72	1.14	2.37	0.31
16/2/11 1.00	1.49	0.99	1.84	0.28
16/2/11 2.00	1.57	0.94	1.56	0.26
16/2/11 3.00	1.89	0.83	1.34	0.32
16/2/11 4.00	1.82	0.95	1.53	0.12
16/2/11 5.00	1.45	1.05	1.57	0.24
16/2/11 6.00	1.69	1.13	1.49	0.59
16/2/11 7.00	1.53	1.20	1.34	0.64
16/2/11 8.00	1.50	0.99	0.76	0.42
16/2/11 9.00	1.72	0.92	0.59	0.45
16/2/11 10.00	1.58	0.86	0.47	0.33
16/2/11 11.00	1.13	0.88	0.41	0.49
16/2/11 12.00	1.84	0.81	0.39	0.55
16/2/11 13.00	1.28	0.83	0.38	0.41
16/2/11 14.00	1.82	0.75	0.31	0.30
16/2/11 15.00	1.76	0.83	0.38	0.21
16/2/11 16.00	1.69	0.87	0.37	0.19
16/2/11 17.00	1.67	0.86	0.38	0.16
16/2/11 18.00	1.49	0.88	0.47	0.15
16/2/11 19.00	1.80	0.84	0.51	0.31
16/2/11 20.00	1.12	0.88	0.72	0.43
16/2/11 21.00	1.66	0.81	0.86	0.29

d-m-yy hh.mm	Sodium	Regional transport	NO_x conversion	Vehicular traffic
16/2/11 22.00	1.83	0.79	0.96	0.42
16/2/11 23.00	1.81	0.68	0.58	0.46
17/2/11 0.00	1.51	0.70	0.60	0.57
17/2/11 1.00	1.86	0.61	0.67	0.48
17/2/11 2.00	1.64	0.66	0.66	0.43
17/2/11 3.00	1.78	0.59	0.49	0.33
17/2/11 4.00	1.83	0.56	0.53	0.28
17/2/11 5.00	1.45	0.60	0.50	0.38
17/2/11 6.00	1.59	0.58	0.53	0.43
17/2/11 7.00	1.76	0.56	0.65	0.41
17/2/11 8.00	1.58	0.58	0.61	0.73
17/2/11 9.00	1.50	0.66	0.69	0.60
17/2/11 10.00	1.83	0.65	0.74	0.67
17/2/11 11.00	1.54	0.64	0.70	0.64
17/2/11 12.00	1.45	0.63	0.71	0.58
17/2/11 13.00	1.50	0.61	0.74	0.75
17/2/11 14.00	1.73	0.59	0.78	0.63
17/2/11 15.00	1.76	0.61	0.80	0.55
17/2/11 16.00	1.81	0.64	0.83	0.43
17/2/11 17.00	1.74	0.63	0.74	0.58
17/2/11 18.00	1.75	0.64	0.76	0.43
17/2/11 19.00	1.53	0.73	0.84	0.20
17/2/11 20.00	1.78	0.81	1.08	0.26
17/2/11 21.00	1.64	0.75	0.97	0.33
17/2/11 22.00	1.75	0.68	0.83	0.21
17/2/11 23.00	1.65	0.74	0.86	0.27
18/2/11 0.00	1.58	0.77	1.02	0.24
18/2/11 1.00	1.45	0.78	1.06	0.31
18/2/11 2.00	1.75	0.75	1.04	0.37
18/2/11 3.00	1.76	0.76	1.16	0.27
18/2/11 4.00	1.39	0.74	1.18	0.44
18/2/11 5.00	1.76	0.73	1.15	0.48
18/2/11 6.00	1.60	0.78	1.25	0.44
18/2/11 7.00	1.50	0.83	1.29	0.42
18/2/11 8.00	1.73	0.84	1.25	0.60
18/2/11 9.00	1.63	0.80	0.94	0.44
18/2/11 10.00	1.38	0.79	0.66	0.52
18/2/11 11.00	1.79	0.71	0.45	0.74
18/2/11 12.00	1.85	0.69	0.37	0.62
18/2/11 13.00	1.83	0.69	0.39	0.57
18/2/11 14.00	1.73	0.71	0.41	0.67
18/2/11 15.00	1.73	0.68	0.36	0.45
18/2/11 16.00	1.66	0.63	0.32	0.41
18/2/11 17.00	1.61	0.63	0.36	0.43
18/2/11 18.00	1.67	0.61	0.32	0.74
18/2/11 19.00	1.71	0.60	0.30	0.87
18/2/11 20.00	1.71	0.68	0.37	0.84
18/2/11 21.00	1.43	0.76	0.38	0.88
18/2/11 22.00	1.41	0.66	0.30	0.89
18/2/11 23.00	1.54	0.61	0.27	0.83
19/2/11 0.00	1.48	0.60	0.23	0.78
19/2/11 1.00	1.35	0.59	0.28	0.80
19/2/11 2.00	1.76	0.58	0.44	0.80
19/2/11 3.00	1.50	0.59	0.36	0.75
19/2/11 4.00	1.67	0.53	0.22	0.87
19/2/11 5.00	1.85	0.53	0.25	0.88
19/2/11 6.00	1.51	0.56	0.26	0.87
19/2/11 7.00	1.72	0.54	0.20	1.20
19/2/11 8.00	1.74	0.56	0.26	1.55
19/2/11 9.00	1.39	0.72	0.53	1.33
19/2/11 10.00	1.88	0.79	1.09	0.81
19/2/11 11.00	1.92	0.82	1.37	0.64
19/2/11 12.00	1.75	0.85	1.52	0.51
19/2/11 13.00	1.96	0.88	1.56	0.26

d-m-yy hh.mm	Sodium	Regional transport	NO_x conversion	Vehicular traffic
19/2/11 14.00	1.91	0.81	1.33	0.20
19/2/11 15.00	1.73	0.74	1.14	0.26
19/2/11 16.00	1.79	0.74	0.97	0.36
19/2/11 17.00	1.88	0.70	0.82	0.61
19/2/11 18.00	1.91	0.68	0.77	0.90
19/2/11 19.00	1.99	0.68	0.71	1.33
19/2/11 20.00	1.98	0.70	0.66	1.93
19/2/11 21.00	2.00	0.73	0.63	2.49
19/2/11 22.00	2.11	0.74	0.57	2.96
19/2/11 23.00	1.96	0.66	0.54	3.01
20/2/11 0.00	1.93	0.65	0.58	2.83
20/2/11 1.00	2.01	0.62	0.59	2.30
20/2/11 2.00	1.89	0.62	0.69	2.12
20/2/11 3.00	1.83	0.63	0.67	1.95
20/2/11 4.00	1.64	0.69	0.66	1.74
20/2/11 5.00	2.01	0.70	0.69	1.51
20/2/11 6.00	1.77	0.79	0.79	1.59
20/2/11 7.00	1.91	0.72	0.97	1.21
20/2/11 8.00	1.97	0.72	1.09	1.47
20/2/11 9.00	1.90	0.73	0.92	1.43
20/2/11 10.00	1.80	0.72	0.95	1.29
20/2/11 11.00	2.07	0.72	0.94	1.00
20/2/11 12.00	1.95	0.77	0.88	0.99
20/2/11 13.00	1.78	0.81	0.71	0.96
20/2/11 14.00	1.91	0.84	0.63	0.61
20/2/11 15.00	1.90	0.86	0.69	0.52
20/2/11 16.00	1.74	0.86	0.64	0.50
20/2/11 17.00	1.83	0.83	0.70	0.71
20/2/11 18.00	1.81	0.83	0.67	0.55
20/2/11 19.00	1.68	0.81	0.56	0.30
20/2/11 20.00	1.82	0.76	0.62	0.31
20/2/11 21.00	1.57	0.75	0.65	0.35
20/2/11 22.00	1.77	0.70	0.56	0.57
20/2/11 23.00	1.79	0.69	0.66	0.29
21/2/11 0.00	1.64	0.70	0.65	0.26
21/2/11 1.00	1.69	0.64	0.59	0.44
21/2/11 2.00	1.78	0.64	0.56	0.26
21/2/11 3.00	1.64	0.64	0.45	0.28
21/2/11 4.00	1.36	0.64	0.34	0.44
21/2/11 5.00	1.67	0.61	0.41	0.45
21/2/11 6.00	1.52	0.64	0.60	0.36
21/2/11 7.00	1.70	0.64	0.64	0.44
21/2/11 8.00	1.71	0.74	1.03	0.53
21/2/11 9.00	1.58	0.85	1.18	0.50
21/2/11 10.00	0.03	1.01	1.16	0.85
21/2/11 11.00	0.03	1.22	1.05	0.91
21/2/11 12.00	0.03	1.08	0.88	0.93
21/2/11 13.00	0.03	1.06	0.76	0.78
21/2/11 14.00	0.03	1.04	0.69	0.88
21/2/11 15.00	0.03	1.04	0.72	0.64
21/2/11 16.00	0.03	1.04	0.75	0.67
21/2/11 17.00	0.03	1.01	0.64	0.62
21/2/11 18.00	0.03	0.97	0.62	0.77
21/2/11 19.00	0.03	1.00	0.60	1.30
21/2/11 20.00	0.03	0.99	0.32	1.03
21/2/11 21.00	0.03	1.11	0.29	1.05
21/2/11 22.00	0.03	1.15	0.28	0.79
21/2/11 23.00	0.03	1.17	0.25	1.11
22/2/11 0.00	0.03	1.22	0.28	0.97
22/2/11 1.00	0.03	1.16	0.26	1.09
22/2/11 2.00	0.03	1.14	0.38	1.11
22/2/11 3.00	0.03	1.01	0.42	1.22
22/2/11 4.00	0.03	0.92	0.43	1.18
22/2/11 5.00	0.03	0.95	0.48	1.27

d-m-yy hh.mm	Sodium	Regional transport	NO_x conversion	Vehicular traffic
22/2/11 6.00	0.17	1.15	0.56	1.45
22/2/11 7.00	0.03	1.08	0.56	1.32
22/2/11 8.00	0.03	0.99	0.51	1.75
22/2/11 9.00	0.03	1.16	0.50	1.33
22/2/11 10.00	0.03	1.20	0.48	0.78
22/2/11 11.00	0.03	1.16	0.42	0.71
22/2/11 12.00	0.03	1.21	0.42	0.66
22/2/11 13.00	0.03	1.26	0.44	0.49
22/2/11 14.00	0.03	1.23	0.36	0.48
22/2/11 15.00	0.03	1.32	0.40	0.45
22/2/11 17.00	0.03	1.24	0.41	0.49
22/2/11 18.00	0.03	1.30	0.43	0.56
22/2/11 19.00	0.03	1.28	0.41	0.53
22/2/11 20.00	0.03	1.24	0.43	0.59
22/2/11 21.00	0.03	1.25	0.44	0.58
22/2/11 22.00	0.03	1.23	0.44	0.69
22/2/11 23.00	0.03	1.23	0.49	0.57
23/2/11 0.00	0.03	1.19	0.54	0.45
23/2/11 1.00	0.03	1.19	0.48	0.59
23/2/11 2.00	0.03	1.37	0.45	0.39
23/2/11 3.00	0.03	1.32	0.52	0.35
23/2/11 4.00	0.03	1.23	0.52	0.31
23/2/11 5.00	0.03	1.23	0.54	0.42
23/2/11 6.00	0.03	1.30	0.60	0.43
23/2/11 7.00	0.03	1.33	0.59	0.50
23/2/11 8.00	0.03	1.24	0.59	0.52
23/2/11 9.00	0.03	1.35	0.66	0.59
23/2/11 10.00	0.03	1.34	0.62	0.50
23/2/11 11.00	0.03	1.24	0.55	0.46
23/2/11 12.00	0.03	1.23	0.53	0.41
23/2/11 13.00	0.03	1.19	0.51	0.42
23/2/11 14.00	0.03	1.15	0.49	0.47
23/2/11 15.00	0.15	1.11	0.45	0.44
23/2/11 16.00	0.03	1.05	0.40	0.48
23/2/11 17.00	0.34	1.03	0.37	0.50
23/2/11 18.00	0.03	1.06	0.40	0.76
23/2/11 19.00	0.03	1.11	0.43	1.02
23/2/11 20.00	0.03	1.24	0.45	0.96
23/2/11 21.00	0.03	1.23	0.41	1.06
23/2/11 22.00	0.03	1.17	0.48	0.92
23/2/11 23.00	0.03	1.11	0.39	1.19
24/2/11 0.00	0.03	1.07	0.35	1.07
24/2/11 1.00	0.03	1.12	0.38	1.06
24/2/11 2.00	0.04	1.10	0.38	1.29
24/2/11 3.00	0.07	1.25	0.42	1.09
24/2/11 4.00	0.18	1.14	0.43	1.00
24/2/11 5.00	0.19	1.17	0.45	0.88
24/2/11 6.00	0.23	1.13	0.46	1.03
24/2/11 7.00	0.20	1.10	0.46	1.26
24/2/11 8.00	0.21	1.14	0.54	1.56
24/2/11 9.00	0.14	1.26	0.68	1.17
24/2/11 10.00	0.03	1.33	0.62	0.91
24/2/11 11.00	0.03	1.31	0.67	0.61
24/2/11 12.00	0.03	1.31	0.72	0.49
24/2/11 13.00	0.03	1.29	0.79	0.54
24/2/11 14.00	0.03	1.29	0.84	0.48
24/2/11 15.00	0.03	1.25	0.88	0.43
24/2/11 16.00	0.03	1.10	0.70	0.58
24/2/11 17.00	0.03	1.08	0.65	0.63
24/2/11 18.00	0.03	1.15	0.70	0.98
24/2/11 19.00	0.03	1.27	0.77	1.12
24/2/11 20.00	0.03	1.23	0.76	1.07
24/2/11 21.00	0.03	1.30	0.74	1.62
24/2/11 22.00	0.03	1.21	0.75	1.53

d-m-yy hh.mm	Sodium	Regional transport	NO_x conversion	Vehicular traffic
24/2/11 23.00	0.03	1.23	0.73	1.46
25/2/11 0.00	0.03	1.12	0.69	1.28
25/2/11 1.00	0.03	1.11	0.66	1.35
25/2/11 2.00	0.03	1.06	0.59	1.50
25/2/11 3.00	0.03	1.03	0.56	1.28
25/2/11 4.00	0.03	1.00	0.50	1.02
25/2/11 5.00	0.03	0.99	0.48	1.13
25/2/11 6.00	0.03	1.10	0.58	1.68
25/2/11 7.00	0.03	0.96	0.41	1.45
25/2/11 8.00	0.03	0.94	0.43	2.05
25/2/11 9.00	0.03	1.08	0.54	1.66
25/2/11 10.00	0.03	1.10	0.62	0.92
25/2/11 11.00	0.03	0.97	0.44	0.71
25/2/11 12.00	0.03	0.98	0.47	0.63
25/2/11 13.00	0.03	0.84	0.36	0.75
25/2/11 14.00	0.03	0.78	0.32	0.76
25/2/11 15.00	0.03	0.78	0.29	0.79
25/2/11 16.00	0.03	0.71	0.21	0.90
25/2/11 17.00	0.03	0.67	0.16	1.01
25/2/11 18.00	0.03	0.66	0.12	1.21
25/2/11 19.00	0.03	0.75	0.13	1.64
25/2/11 20.00	0.03	0.75	0.12	2.01
25/2/11 21.00	0.03	0.87	0.16	2.26
25/2/11 22.00	0.03	0.78	0.15	1.85
25/2/11 23.00	0.03	0.77	0.04	2.60
26/2/11 0.00	0.03	0.77	0.07	2.60
26/2/11 1.00	0.03	0.71	0.07	2.19
26/2/11 2.00	0.03	0.75	0.11	1.95
26/2/11 3.00	0.03	0.76	0.14	1.83
26/2/11 4.00	0.03	0.78	0.18	1.62
26/2/11 5.00	0.03	0.80	0.21	1.64
26/2/11 6.00	0.03	0.98	0.28	1.62

d-m-yy hh.mm	Sodium	Regional transport	NO_x conversion	Vehicular traffic
26/2/11 7.00	0.03	1.09	0.37	1.48
26/2/11 8.00	0.03	1.20	0.53	1.40
26/2/11 9.00	0.03	1.40	0.53	1.10
26/2/11 10.00	0.03	1.42	0.50	0.67
26/2/11 11.00	0.03	1.25	0.49	0.49
26/2/11 12.00	0.03	1.15	0.53	0.57
26/2/11 13.00	0.03	1.17	0.56	0.57
26/2/11 14.00	0.03	1.13	0.57	0.55
26/2/11 15.00	0.03	1.12	0.67	0.54
26/2/11 16.00	0.03	1.12	0.74	0.48
26/2/11 17.00	0.03	1.10	0.72	0.59
26/2/11 18.00	0.03	1.07	0.70	1.02
26/2/11 19.00	0.03	1.05	0.64	1.93
26/2/11 20.00	0.03	1.03	0.63	2.16
26/2/11 21.00	0.03	1.25	0.59	2.05
26/2/11 22.00	0.03	1.31	0.57	1.72
26/2/11 23.00	0.03	1.26	0.56	1.02
27/2/11 0.00	0.03	1.21	0.59	1.18
27/2/11 1.00	0.03	1.04	0.66	0.91
27/2/11 2.00	0.03	0.97	0.51	1.05
27/2/11 3.00	0.03	0.94	0.52	1.03
27/2/11 4.00	0.03	0.99	0.46	1.02
27/2/11 5.00	0.03	1.10	0.56	1.07
27/2/11 6.00	0.03	1.08	0.56	1.03
27/2/11 7.00	0.03	1.06	0.94	0.95
27/2/11 8.00	0.03	1.08	1.14	0.79
27/2/11 9.00	0.03	1.02	1.06	0.54
27/2/11 10.00	0.03	0.92	0.89	0.61
27/2/11 11.00	0.03	0.90	0.85	0.73
27/2/11 12.00	0.03	0.93	0.89	0.62
27/2/11 13.00	0.03	1.01	1.07	0.55
27/2/11 14.00	0.03	0.99	0.93	0.45

d-m-yy hh.mm	Sodium	Regional transport	NO_x conversion	Vehicular traffic
27/2/11 15.00	0.03	0.99	0.96	0.59
27/2/11 16.00	0.03	0.99	0.97	0.69
27/2/11 17.00	0.03	0.93	0.81	0.67
27/2/11 18.00	0.03	0.88	0.67	0.83
27/2/11 19.00	0.03	0.83	0.58	1.02
27/2/11 20.00	0.03	0.81	0.68	1.02
27/2/11 21.00	0.03	0.80	0.98	1.12
27/2/11 22.00	0.03	0.86	1.00	1.09
27/2/11 23.00	0.03	0.88	0.88	0.81
28/2/11 0.00	0.03	0.88	0.91	0.94
28/2/11 1.00	0.03	0.90	1.03	0.87
28/2/11 2.00	0.03	1.12	1.00	0.66
28/2/11 3.00	0.03	0.97	0.82	0.58
28/2/11 4.00	0.03	0.90	0.72	0.64
28/2/11 5.00	0.03	1.14	0.89	0.70
28/2/11 6.00	0.03	1.13	0.90	0.69
28/2/11 7.00	0.03	1.04	0.75	0.78
28/2/11 8.00	0.03	0.82	0.46	0.88
28/2/11 9.00	0.03	0.80	0.35	0.94
28/2/11 10.00	0.03	0.91	0.39	0.96
28/2/11 11.00	0.03	1.10	0.49	0.80
28/2/11 12.00	0.03	1.20	0.57	0.60
28/2/11 13.00	0.03	1.15	0.49	0.71
28/2/11 14.00	0.03	1.11	0.41	0.74
28/2/11 15.00	0.03	1.19	0.42	0.80
28/2/11 16.00	0.03	0.56	0.59	1.11
28/2/11 17.00	0.03	1.44	0.44	0.61
28/2/11 18.00	0.03	1.18	0.31	0.90
28/2/11 19.00	0.03	1.31	0.45	0.82
28/2/11 20.00	0.03	1.40	0.59	0.69
28/2/11 21.00	0.03	1.25	0.55	0.66
28/2/11 22.00	0.03	1.21	0.55	0.74
28/2/11 23.00	0.03	1.25	0.68	0.68
1/3/11 0.00	0.03	1.18	0.67	0.73
1/3/11 1.00	0.03	1.11	0.62	0.57
1/3/11 2.00	0.03	1.11	0.59	0.66
1/3/11 3.00	0.03	1.22	0.55	0.55
1/3/11 4.00	0.03	1.30	0.60	0.27
1/3/11 5.00	0.03	1.34	0.49	0.48
1/3/11 6.00	0.03	1.31	0.54	0.57
1/3/11 7.00	0.03	1.41	0.60	0.62
1/3/11 8.00	0.03	1.40	0.48	0.76
1/3/11 9.00	0.03	1.44	0.42	0.82
1/3/11 10.00	0.03	1.47	0.45	0.94
1/3/11 11.00	0.03	1.65	0.50	0.96
1/3/11 12.00	0.07	1.75	0.38	0.66
1/3/11 13.00	0.09	1.68	0.30	0.42
1/3/11 14.00	0.10	1.60	0.22	0.66
1/3/11 15.00	0.09	1.50	0.23	0.50
1/3/11 16.00	0.07	1.44	0.15	0.77
1/3/11 17.00	0.22	1.48	0.18	0.48
1/3/11 18.00	0.27	1.49	0.14	0.67
1/3/11 19.00	0.32	1.49	0.13	0.69
1/3/11 20.00	0.23	1.43	0.13	0.75
1/3/11 21.00	0.26	1.66	0.21	0.39
1/3/11 22.00	0.19	1.65	0.23	0.21
1/3/11 23.00	0.20	1.61	0.22	0.25
2/3/11 0.00	0.03	1.38	0.24	0.18
2/3/11 1.00	0.03	1.28	0.36	0.22
2/3/11 2.00	0.03	1.12	0.41	0.43
2/3/11 3.00	0.03	1.51	0.39	0.17
2/3/11 4.00	0.03	1.47	0.30	0.07
2/3/11 5.00	0.03	1.29	0.23	0.20
2/3/11 6.00	0.03	1.17	0.21	0.36

d-m-yy hh.mm	Sodium	Regional transport	NO_x conversion	Vehicular traffic
2/3/11 7.00	0.03	1.09	0.20	0.51
2/3/11 8.00	0.03	1.02	0.16	0.58
2/3/11 9.00	0.03	0.99	0.14	0.67
2/3/11 10.00	0.03	0.83	0.11	0.67
2/3/11 11.00	0.03	0.75	0.03	0.92
2/3/11 12.00	0.03	0.81	0.07	0.85
2/3/11 13.00	0.03	0.75	0.04	1.09
2/3/11 14.00	0.03	0.70	0.01	1.17
2/3/11 15.00	0.03	0.77	0.07	1.03
2/3/11 16.00	0.03	0.87	0.15	0.84
2/3/11 17.00	0.03	0.96	0.22	0.78
2/3/11 18.00	0.03	0.94	0.33	0.88
2/3/11 19.00	0.03	0.94	0.34	1.00
2/3/11 20.00	0.03	0.96	0.37	1.04
2/3/11 21.00	0.03	0.98	0.38	1.10
2/3/11 22.00	0.03	1.02	0.43	1.01
2/3/11 23.00	0.03	1.14	0.41	1.15

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